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<p>(21) Application No 9827565.4</p> <p>(22) Date of Filing 16.12.1998</p> <p>(30) Priority Data (31) 97811019 (32) 23.12.1997 (33) EP</p> <p>(71) Applicant(s) Ciba Specialty Chemicals Holding Inc. (Incorporated in Switzerland) Klybeckstrasse 141, 4057 Basel, Switzerland</p> <p>(72) Inventor(s) Francois Gugumus</p> <p>(74) Agent and/or Address for Service M Upschulte Ciba Specialty Chemicals Plc, UK Patents Department, Cleckheaton Road, Low Moor, BRADFORD, West Yorkshire, BD12 0JZ, United Kingdom</p>	<p>(51) INT CL⁶ C08K 13/02 3/00 5/00 // (C08K 5/00 5:098 5:3435 5:3492 5:54) (C08K 13/02 3:20 3:28 5:098 5:3435 5:3492 5:54) (C08K 3/00 3:22 3:26 5:098 5:3435 5:3492 5:54)</p> <p>(52) UK CL (Edition Q) C3K KCZ K111 K124 K127 K201 K210 K211 K221 K230 K241 K244 K251 K252 K254 K270 K274 K277 K284 K281 K282 K294 K297 K298 C3W W207 W208 W216 W217 W218</p> <p>(56) Documents Cited EP 0429731 A1 EP 0212559 A2 US 5350785 A US 5283273 A US 5025051 A</p> <p>(58) Field of Search UK CL (Edition Q) C3K KCZ INT CL⁶ C08K 5/00 5/098 5/34 5/3432 5/3435 5/3437 5/3492 ONLINE: EDOC, PAJ, WPI</p>
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(54) Abstract Title
Stabilizer mixtures comprising a sterically hindered amine

- (57) A stabilizer mixture contains
- (A) a sterically hindered amine compound,
 - (B) an organic salt or inorganic salt of Ca and
 - (C) an organic salt or inorganic salt of Mg or an organic salt or inorganic salt of Zn;
- with the proviso that component (C) is Mg-hydroxide-carbonate, Zn-hydroxide-carbonate or dolomite, when component (B) is calcium stearate.
- Also claimed is a composition comprising a polyolefin and a stabilizer mixture containing
- (A) a sterically hindered amine compound selected from compounds 13, 14, 36-a, 36-b, 36-d, 96-I, 96-II, 101-A, 101-1, 105 and 106 as defined in the specification,
 - (B) an organic or inorganic salt of Ca and
 - (C) an organic or inorganic salt of Mg or an organic or inorganic salt of Zn; with the proviso that the polyolefin is polypropylene, when component (A) is the compound 96-I, 96-II or 100-A.
- The inorganic salt may be an oxide or hydroxide.

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G_{12} , if n_1 is 2, is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or phosphorus-containing acid or a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms, where each dicarboxylic acid may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by one or two $-COOZ_{12}$ groups,

G_{12} , if n_1 is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which may be substituted in the aliphatic, cycloaliphatic or aromatic moiety by $-COOZ_{12}$, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical,

and G_{12} , if n_1 is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

The carboxylic acid radicals mentioned above are in each case taken to mean radicals of the formula $(-CO)_xR$, where x is as defined above, and the meaning of R arises from the definition given.

Alkyl with up to 20 carbon atoms is, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

C_3 - C_8 alkenyl G_{11} can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, or 4-tert-butyl-2-butenyl.

C_3 - C_8 alkynyl G_{11} is preferably propargyl.

C_7 - C_{12} aralkyl G_{11} is, in particular, phenethyl, especially benzyl.

C_1 - C_{18} alkoxy G_{11} is, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy and octadecyloxy. C_6 - C_{12} alkoxy, in particular heptoxy and octoxy, is preferred.

C₅-C₈cycloalkoxy G₁₁ is, for example, cyclopentoxy, cyclohexoxy, cycloheptoxy, cyclooctoxy, cyclodecyloxy and cyclododecyloxy. C₅-C₈cycloalkoxy, in particular cyclopentoxy and cyclohexoxy, is preferred.

C₇-C₉phenylalkoxy is, for example, benzyloxy.

C₁-C₈alkanoyl G₁₁ is, for example, formyl, propionyl, butyryl, octanoyl, but preferably acetyl and C₃-C₅alkenoyl G₁₁ is in particular acryloyl.

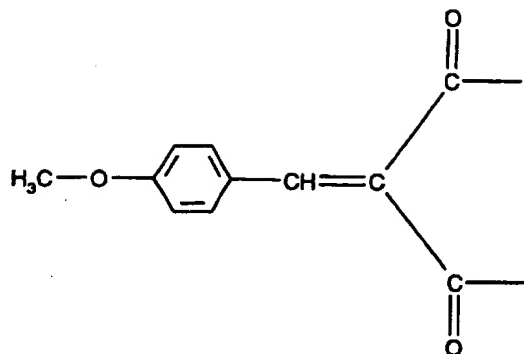
C₁-C₁₆alkanoyloxy G₁₁ is, for example, formyloxy, acetyloxy, propionyloxy, butyryloxy, valeryloxy, lauroyloxy, palmitoyloxy and stearoyloxy.

Examples of several G₁₂ radicals are given below.

If G₁₂ is a monovalent radical of a carboxylic acid, it is, for example, an acetyl, caproyl, stearoyl, acryloyl, methacryloyl, benzoyl or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl radical.

If G₁₂ is a monovalent silyl radical, it is, for example, a radical of the formula $-(C_1H_2)_j-Si(Z')_2Z''$, in which j is an integer in the range from 2 to 5, and Z' and Z'', independently of one another, are C₁-C₄alkyl or C₁-C₄alkoxy.

If G₁₂ is a divalent radical of a dicarboxylic acid, it is, for example, a malonyl, succinyl, glutaryl, adipoyl, suberoyl, sebacoyl, maleoyl, itaconyl, phthaloyl, dibutylmalonyl, dibenzylmalonyl, butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonyl or bicycloheptenedicarbonyl radical or a group of the formula



If G_{12} is a trivalent radical of a tricarboxylic acid, it is, for example, a trimellitoyl, citryl or nitrilotriacetyl radical.

If G_{12} is a tetravalent radical of a tetracarboxylic acid, it is, for example, the tetravalent radical of butane-1,2,3,4-tetracarboxylic acid or of pyromellitic acid.

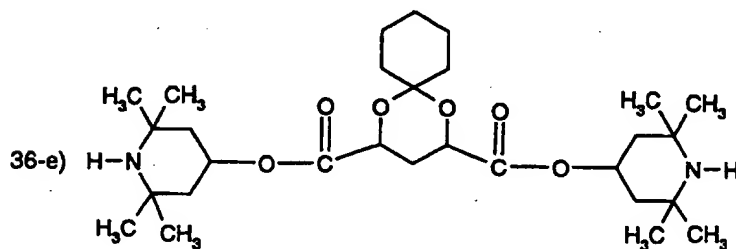
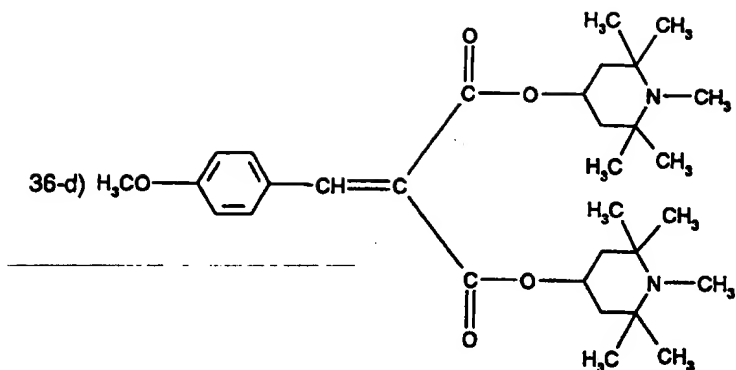
If G_{12} is a divalent radical of a dicarbamic acid, it is, for example, hexamethylenedicarbamoyl or 2,4-toluylenedicarbamoyl radical.

Preference is given to compounds of the formula (Ia) in which G and G_1 are hydrogen, G_{11} is hydrogen or methyl, n_1 is 2 and G_{12} is the diacyl radical of an aliphatic dicarboxylic acid having 4-12 carbon atoms.

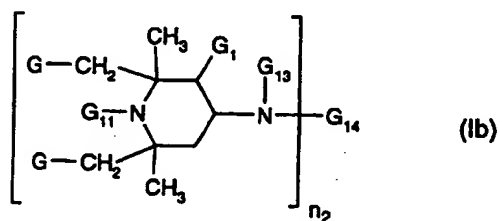
Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 1) 4-hydroxy-2,2,6,6-tetramethylpiperidine
- 2) 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 3) 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 4) 1-(4-tert-butyl-2-butenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 5) 4-stearoyloxy-2,2,6,6-tetramethylpiperidine
- 6) 1-ethyl-4-salicyloyloxy-2,2,6,6-tetramethylpiperidine
- 7) 4-methacryloyloxy-1,2,2,6,6-pentamethylpiperidine
- 8) 1,2,2,6,6-pentamethylpiperidin-4-yl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
- 9) di(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) maleate

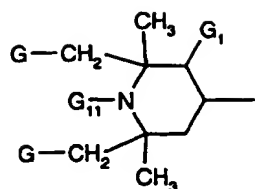
- 10) di(2,2,6,6-tetramethylpiperidin-4-yl) succinate
- 11) di(2,2,6,6-tetramethylpiperidin-4-yl) glutarate
- 12) di(2,2,6,6-tetramethylpiperidin-4-yl) adipate
- 13) di(2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 14) di(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate
- 15) di(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) sebacate
- 16) di(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate
- 17) 1-hydroxy-4-β-cyanoethoxy-2,2,6,6-tetramethylpiperidine
- 18) 1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl acetate
- 19) tri(2,2,6,6-tetramethylpiperidin-4-yl) trimellitate
- 20) 1-acryloyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine
- 21) di(2,2,6,6-tetramethylpiperidin-4-yl) diethylmalonate
- 22) di(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate
- 23) di(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate
- 24) di(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 25) di(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 26) hexane-1',6'-bis(4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine)
- 27) toluene-2',4'-bis-(4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine)
- 28) dimethylbis(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 29) phenyltris(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 30) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 30-a) tris(1-methyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 31) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphate
- 32) phenyl bis(1,2,2,6,6-pentamethylpiperidin-4-yl) phosphonate
- 33) 4-hydroxy-1,2,2,6,6-pentamethylpiperidine
- 34) 4-hydroxy-N-hydroxyethyl-2,2,6,6-tetramethylpiperidine
- 35) 4-hydroxy-N-(2-hydroxypropyl)-2,2,6,6-tetramethylpiperidine
- 36) 1-glycidyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 36-a) 1,2,3,4-tetrakis[2,2,6,6-tetramethylpiperidin-4-yloxy-carbonyl]butane
- 36-b) 1,2,3,4-tetrakis[1,2,2,6,6-pentamethylpiperidin-4-yloxy-carbonyl]butane
- 36-c) 2,2,6,6-tetramethylpiperidin-4-yloxy-carbonyl(C₁₅-C₁₇alkane)



(b') A compound of the formula (Ib)

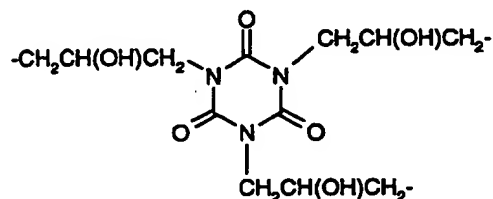


in which n_2 is the number 1, 2 or 3, G, G_1 and G_{11} are as defined under (a'), G_{13} is hydrogen, C_1 - C_{12} alkyl, C_2 - C_5 hydroxyalkyl, C_5 - C_7 cycloalkyl, C_7 - C_8 aralkyl, C_1 - C_{18} alkanoyl, C_3 - C_5 alkenoyl, benzoyl or a group of the formula



and G_{14} , if n_2 is 1, is hydrogen, C_1 - C_{18} alkyl, C_3 - C_8 alkenyl, C_5 - C_7 cycloalkyl, C_1 - C_4 alkyl which is substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamide group, glycidyl, a group of the formula $-CH_2-CH(OH)-Z$ or of the formula $-CONH-Z$, in which Z is hydrogen, methyl or phenyl;

G_{14} , if n_2 is 2, is C_2 - C_{12} alkylene, C_6 - C_{12} arylene, xylylene, a $-CH_2-CH(OH)-CH_2$ group or a $-CH_2-CH(OH)-CH_2-O-D-O-$ group, in which D is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene, or, provided that G_{13} is not alkanoyl, alkenoyl or benzoyl, G_{14} can alternatively be 1-oxo- C_2 - C_{12} alkylene, a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or alternatively the group $-CO-$,
 G_{14} , if n_2 is 3, is a group



or, if n_2 is 1, G_{13} and G_{14} together can be the divalent radical of an aliphatic, cycloaliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

Some examples for the radicals G_{13} , G_{14} and D are given below.

Any alkyl substituents are as defined above for (a').

Any C_5 - C_7 cycloalkyl substituents are, in particular, cyclohexyl.

C_7 - C_8 aralkyl G_{13} is, in particular, phenylethyl or especially benzyl.

C_2-C_5 hydroxyalkyl G_{13} is, in particular, 2-hydroxyethyl or 2-hydroxypropyl.

C_1-C_{18} alkanoyl G_{13} is, for example, formyl, acetyl, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl, octadecanoyl, but preferably acetyl, and C_3-C_5 alkenoyl G_{13} is, in particular, acryloyl.

C_2-C_8 alkenyl G_{14} is, for example, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl or 2-octenyl.

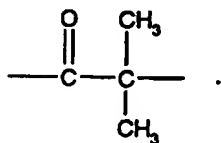
G_{14} as a hydroxyl-, cyano-, alkoxycarbonyl- or carbamide-substituted C_1-C_4 alkyl can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-cyanoethyl, methoxycarbonylmethyl, 2-ethoxycarbonylethyl, 2-aminocarbonylpropyl or 2-(dimethylaminocarbonyl)ethyl.

Any C_2-C_{12} alkylene radicals are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

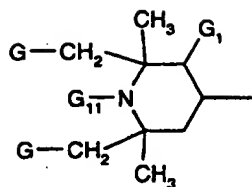
Any C_6-C_{15} arylene substituents are, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C_6-C_{12} cycloalkylene is, in particular, cyclohexylene.

G_{14} as 1-oxo- C_2-C_{12} alkylene is preferably a group



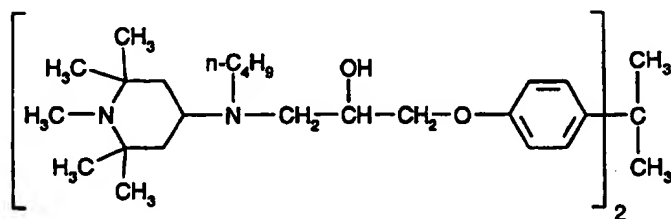
Preference is given to compounds of the formula (Ib) in which n_2 is 1 or 2, G and G_1 are hydrogen, G_{11} is hydrogen or methyl, G_{13} is hydrogen, C_1-C_{12} alkyl or a group of the formula



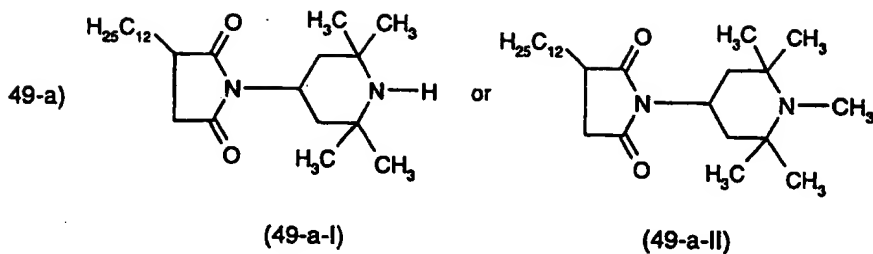
and G_{14} , in the case where $n=1$, is hydrogen or C_1 - C_{12} alkyl, and, in the case where $n=2$, is C_2 - C_8 alkylene or 1-oxo- C_2 - C_8 alkylene.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 37) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diamine
- 38) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diacetamide
- 39) bis(2,2,6,6-tetramethylpiperidin-4-yl)amine
- 40) 4-benzoylamino-2,2,6,6-tetramethylpiperidine
- 41) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyladipamide
- 42) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dicyclohexyl-2-hydroxypropylene-1,3-diamine
- 43) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylenediamine
- 44) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)succinamide
- 45) bis(2,2,6,6-tetramethylpiperidin-4-yl) N-(2,2,6,6-tetramethylpiperidin-4-yl)-β-aminodipropionate
- 46) The compound of the formula



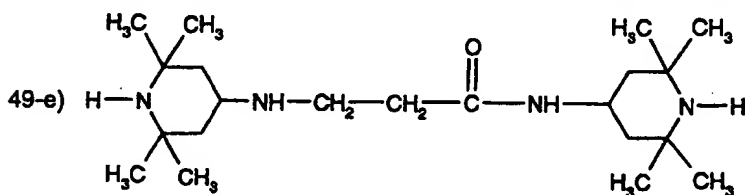
- 47) 4-(bis-2-hydroxyethylamino)-1,2,2,6,6-pentamethylpiperidine
- 48) 4-(3-methyl-4-hydroxy-5-tert-butyl-benzamido)-2,2,6,6-tetramethylpiperidine
- 49) 4-methacrylamido-1,2,2,6,6-pentamethylpiperidine



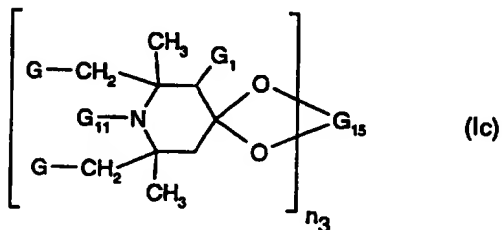
49-b) N,N',N''-tris[2,2,6,6-tetramethylpiperidin-4-ylamino(2-hydroxypropylene)]isocyanurate

49-c) 2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-2-(2,2,6,6-tetramethylpiperidin-4-ylaminocarbonyl)propane

49-d) 1,6-bis[N-(2,2,6,6-tetramethylpiperidin-4-yl)formylamino]hexane



(c') A compound of the formula (Ic)



in which n_3 is the number 1 or 2, G, G_1 and G_{11} are as defined under (a'), and G_{15} , if n_3 is 1, is C_2 - C_8 alkylene, C_2 - C_8 hydroxyalkylene or C_4 - C_{22} acyloxyalkylene, and if n_3 is 2, G_{15} is the $(-CH_2)_2C(CH_2)_2$ group.

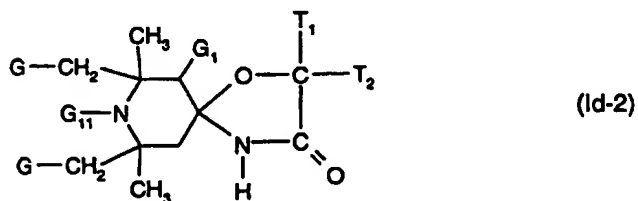
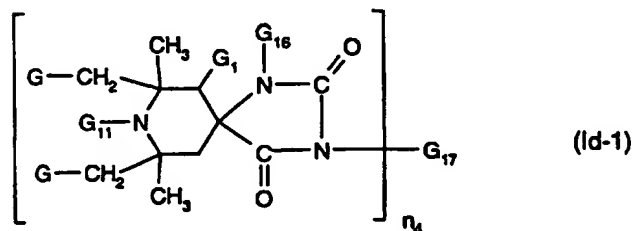
C_2 - C_8 alkylene or C_2 - C_8 hydroxyalkylene G_{15} is, for example, ethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

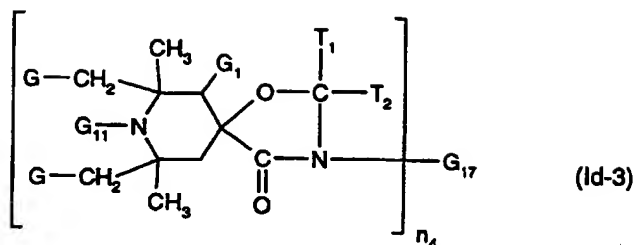
C_4 - C_{22} acyloxyalkylene G_{15} is, for example, 2-ethyl-2-acetoxymethylpropylene.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 50) 9-aza-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 51) 9-aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]undecane
- 52) 8-aza-2,7,7,8,9,9-hexamethyl-1,4-dioxaspiro[4.5]decane
- 53) 9-aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]undecane
- 54) 9-aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 55) 2,2,6,6-tetramethylpiperidine-4-spiro-2'-(1',3'-dioxane)-5'-spiro-5''-(1'',3''-dioxane)-2''-spiro-4'''-(2'''',2'''',6'''',6'''-tetramethylpiperidine)

(d') A compound of the formula (Id-1), (Id-2) or (Id-3),





in which n_4 is the number 1 or 2, G, G_1 and G_{11} are as defined under (a'), G_{18} is hydrogen, C_1 - C_{12} alkyl, allyl, benzyl, glycidyl or C_2 - C_6 alkoxyalkyl, and G_{17} , if n_4 is 1, is hydrogen, C_1 - C_{12} alkyl, C_3 - C_5 alkenyl, C_7 - C_9 aralkyl, C_5 - C_7 cycloalkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_6 - C_{10} aryl, glycidyl or a group of the formula $-(CH_2)_p-COO-Q$ or $-(CH_2)_p-O-CO-Q$, in which p is 1 or 2, and Q is C_1 - C_4 alkyl or phenyl, and G_{17} , if n is 2, is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_6 - C_{12} arylene, a group of the formula $-CH_2-CH(OH)-CH_2-O-D'-O-CH_2-CH(OH)-CH_2-$, in which D' is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene or a group of the formula $-CH_2CH(OD'')CH_2-(OCH_2-CH(OD''))CH_2)_2-$, in which D'' is hydrogen, C_1 - C_{18} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl, T_1 and T_2 , independently of one another, are hydrogen, C_1 - C_{18} alkyl or unsubstituted or halogen- or C_1 - C_4 alkyl-substituted C_6 - C_{10} aryl or C_7 - C_9 aralkyl, or T_1 and T_2 together with the carbon atom bonding them form a C_5 - C_{14} cycloalkane ring.

A compound of the formula (Id-3) is preferred.

Some examples of the several variables in the formulae (Id-1), (Id-2) and (Id-3) are given below.

Any C_1 - C_{12} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any C_1 - C_{18} alkyl substituents can be, for example, the abovementioned groups and in addition, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any C₂-C₆alkoxyalkyl substituents are, for example, methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxypropyl.

C₃-C₅alkenyl G₁₇ is, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

C₇-C₈aralkyl G₁₇, T₁ and T₂ are, in particular, phenethyl or especially benzyl. If T₁ and T₂ together with the carbon atom form a cycloalkane ring, this can be, for example, a cyclopentane, cyclohexane, cyclooctane or cyclododecane ring.

C₂-C₄hydroxyalkyl G₁₇ is, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

C₆-C₁₀aryl G₁₇, T₁ and T₂ are, in particular, phenyl or α - or β -naphthyl, which are unsubstituted or substituted by halogen or C₁-C₄alkyl.

C₂-C₁₂alkylene G₁₇ is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

C₄-C₁₂alkenylene G₁₇ is, in particular, 2-butenylene, 2-pentenylene or 3-hexenylene.

C₆-C₁₂arylene G₁₇ is, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C₂-C₁₂alkanoyl D'' is, for example, proplonyl, butyryl, octanoyl, dodecanoyl, but preferably acetyl.

C₂-C₁₀alkylene, C₆-C₁₅arylene or C₆-C₁₂cycloalkylene D' have, for example, one of the definitions given for D under (b').

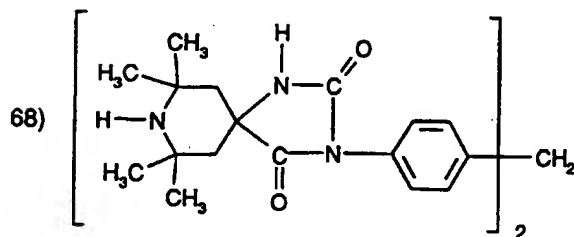
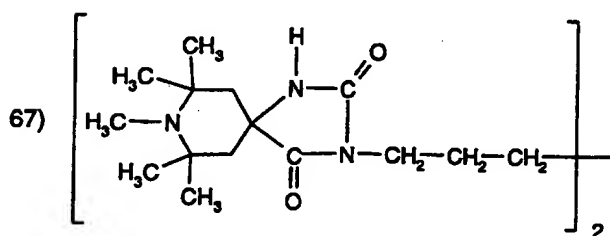
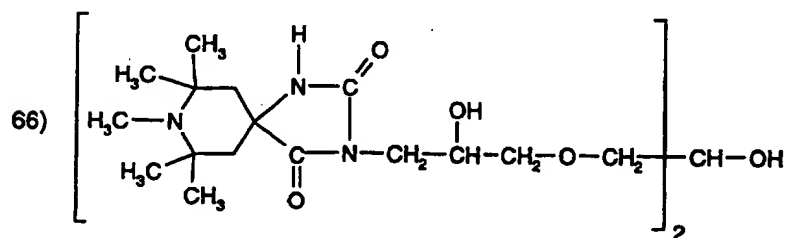
Examples of polyalkylpiperidine compounds from this class are the following compounds:

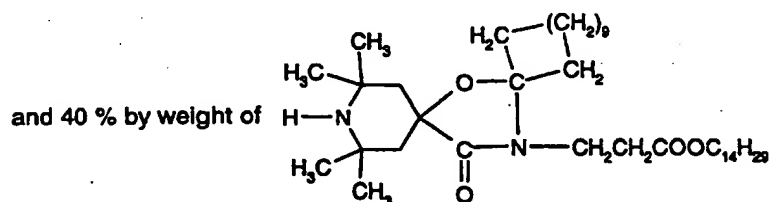
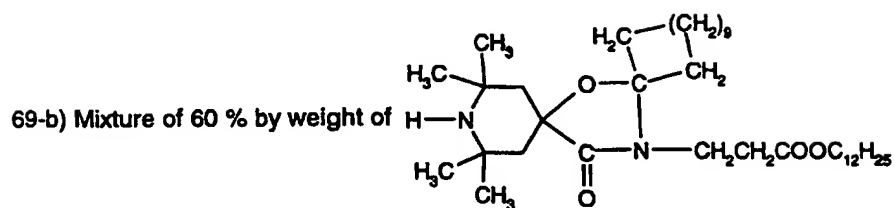
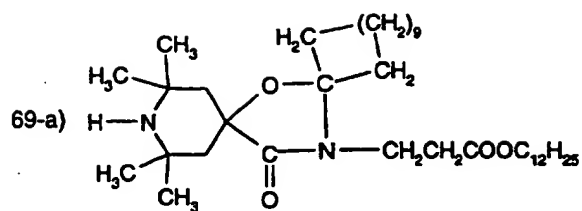
56) 3-benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

57) 3-n-octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

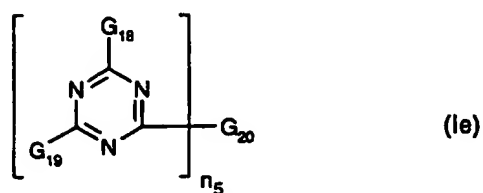
- 58) 3-allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]decane-2,4-dione
 59) 3-glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione
 60) 1,3,7,7,8,9,9-heptamethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione
 61) 2-isopropyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
 62) 2,2-dibutyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
 63) 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2]heneicosane
 64) 2-butyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-oxospiro[4.5]decane and preferably:
 65) 8-acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

and the compounds of the following formulae:

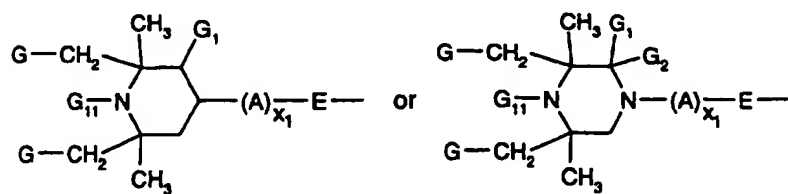




(e') A compound of the formula (Ie)



in which n_5 is the number 1 or 2, and G_{18} is a group of the formula



in which G and G₁₁ are as defined under (a'), and G₁ and G₂ are hydrogen, methyl or, together, are a substituent =O,

E is -O- or -ND^{'''}-,

A is C₂-C₆alkylene or -(CH₂)₃-O- and

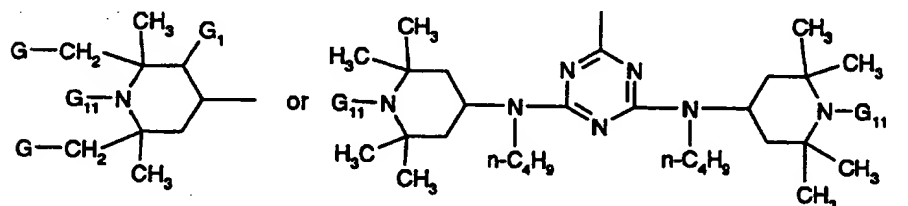
x₁ is the number 0 or 1,

D^{'''} is hydrogen, C₁-C₁₂alkyl, C₂-C₅hydroxyalkyl or C₅-C₇cycloalkyl,

G₁₉ is identical to G₁₈ or is one of the groups -N(G₂₁)(G₂₂), -OG₂₃, -N(H)(CH₂OG₂₃) or -N(CH₂OG₂₃)₂,

G₂₀, if n = 1, is identical to G₁₈ or G₁₉ and, if n = 2, is an -E-D^V-E- group, in which D^V is C₂-C₆alkylene or C₂-C₈alkylene which is interrupted by 1 or 2 -NG₂₁- groups,

G₂₁ is C₁-C₁₂alkyl, cyclohexyl, benzyl or C₁-C₄-hydroxyalkyl or a group of the formula



G₂₂ is C₁-C₁₂alkyl, cyclohexyl, benzyl or C₁-C₄hydroxyalkyl, and

G₂₃ is hydrogen, C₁-C₁₂alkyl or phenyl, or G₂₁ and G₂₂ together are C₄-C₅alkylene or C₄-C₅oxaalkylene, for example -CH₂CH₂-O-CH₂CH₂-, or a group of the formula -CH₂CH₂-N(G₁₁)-CH₂CH₂-.

Some examples of the several variables in the formula (Ie) are given below.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

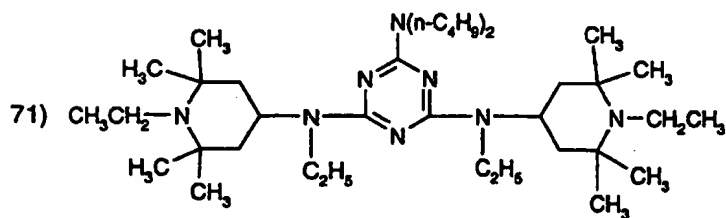
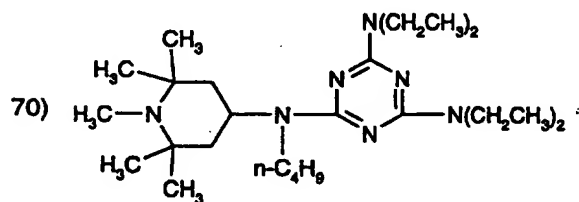
Any hydroxyalkyl substituents are, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

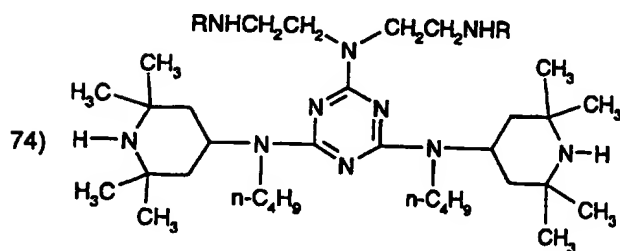
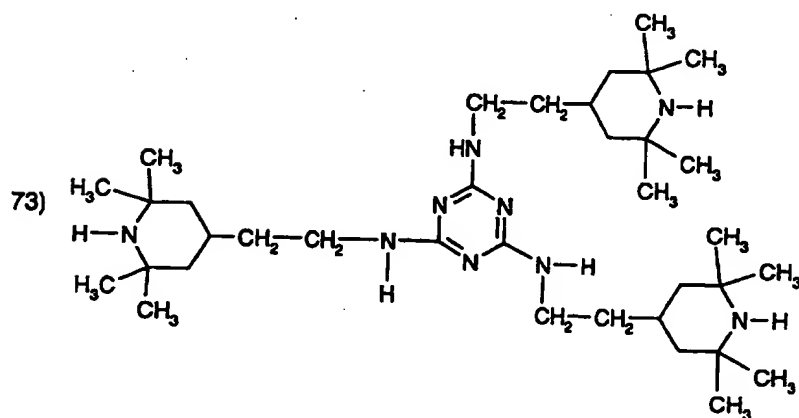
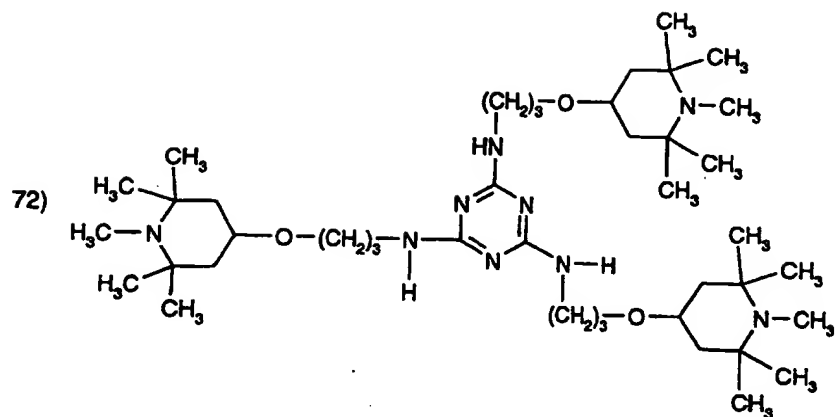
Any C₅-C₇-cycloalkyl substituents are, for example, cyclopentyl, cyclohexyl or cycloheptyl. Cyclohexyl is preferred.

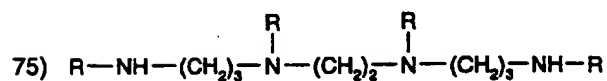
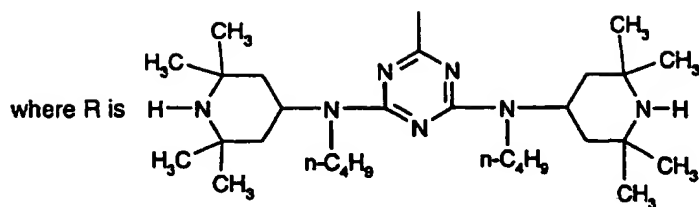
C₂-C₆alkylene A is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

If G₂₁ and G₂₂ together are C₄-C₅alkylene or oxaalkylene, they are, for example, tetramethylene, pentamethylene or 3-oxapentamethylene.

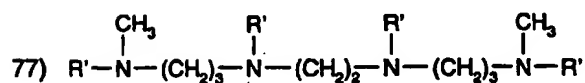
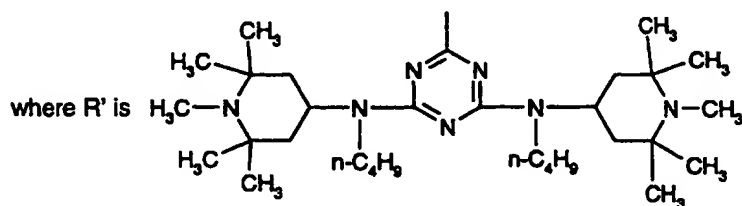
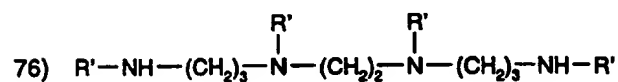
Examples of polyalkylpiperidine compounds from this class are the compounds of the following formulae:



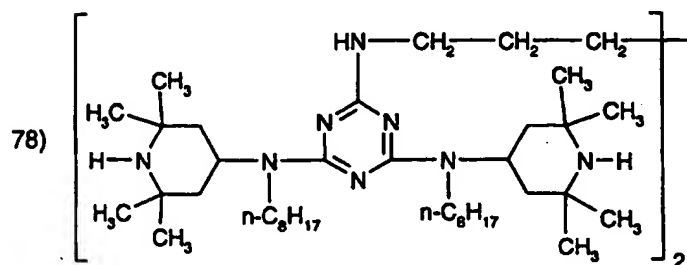


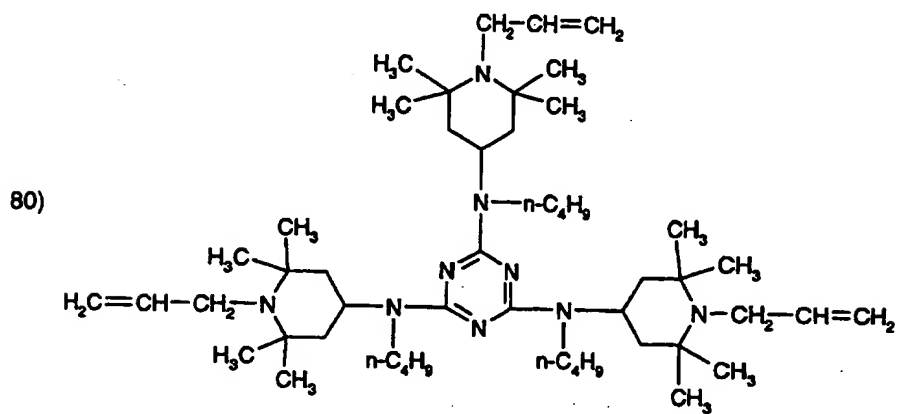
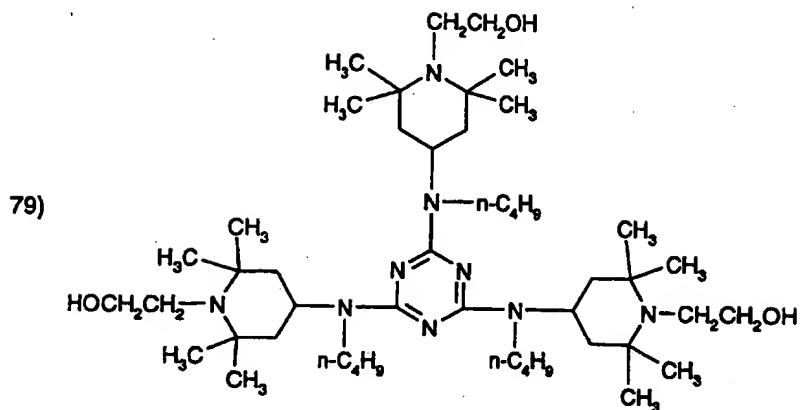


where R has the same meaning as in compound 74.

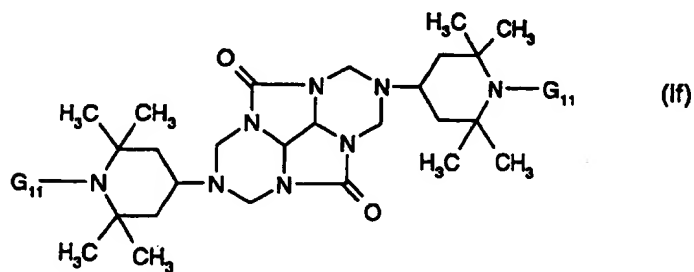


where R' has the same meaning as in compound 76.



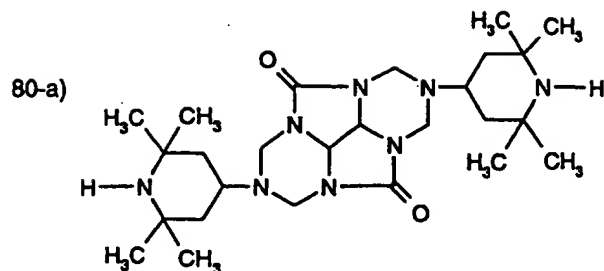


(f') A compound of the formula (If)



wherein G_{11} is as defined under (a').

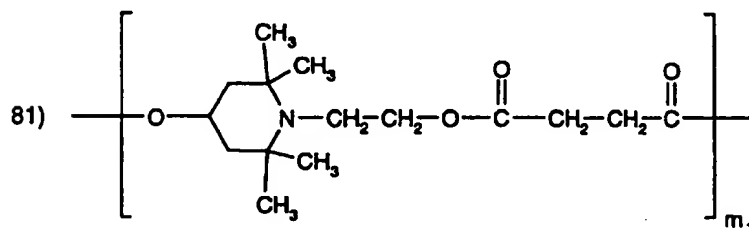
A preferred example from this class is the following compound:

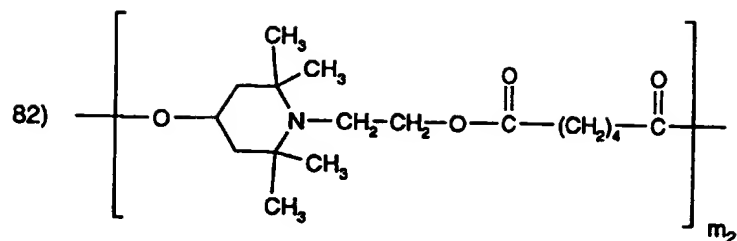


(g') Oligomeric or polymeric compounds whose recurring structural unit contains a 2,2,6,6-tetraalkylpiperidiny radical, in particular polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and copolymers thereof which contain such radicals.

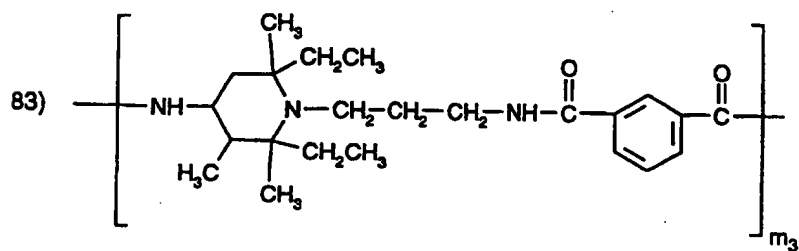
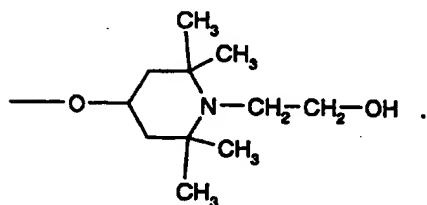
Examples of 2,2,6,6-polyalkylpiperidine compounds from this class are the compounds of the following formulae, where m_1 to m_{14} is a number from 2 to about 200, preferably 2 to 100, for example 2 to 50, 2 to 40 or 3 to 40 or 4 to 10.

The meanings of the end groups which saturate the free valences in the oligomeric or polymeric compounds listed below depend on the processes used for the preparation of said compounds. The end groups can also in addition be modified after the synthesis of the compounds.





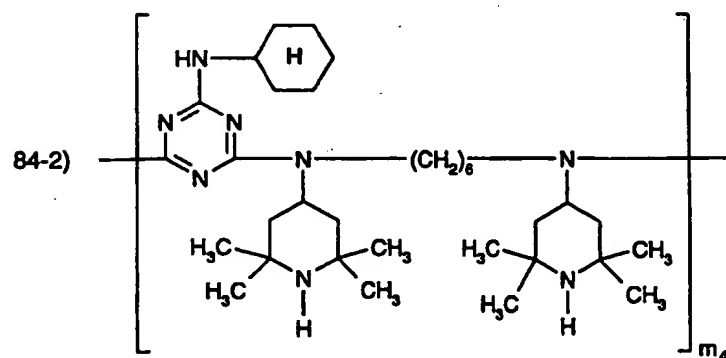
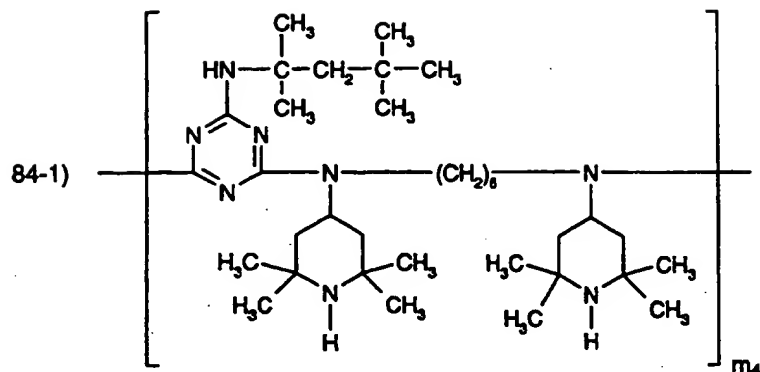
In the compounds 81 and 82, the end group bonded to the -O- can be, for example, hydrogen or a group $-\text{CO}-(\text{CH}_2)_2-\text{COO}-\text{Y}$ or $-\text{CO}-(\text{CH}_2)_4-\text{COO}-\text{Y}$, respectively, with Y being hydrogen or C₁-C₄alkyl and the end group bonded to the diacyl can be, for example, -O-Y or a group



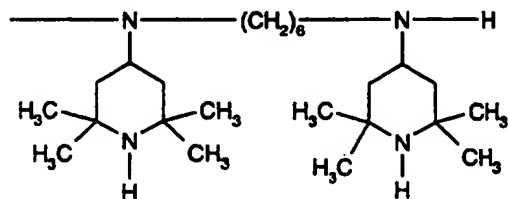
In the compound 83, the end group bonded to the amino residue can be, for example, a



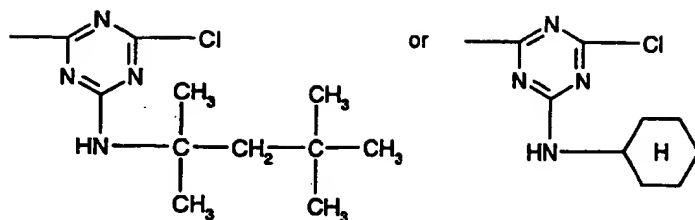
for example, Cl.



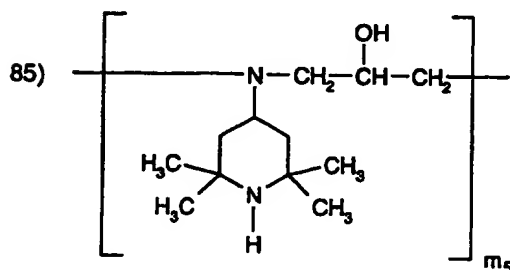
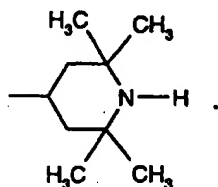
In the compounds 84-1 and 84-2, the end group bonded to the triazine residue can be, for example, chlorine or a group



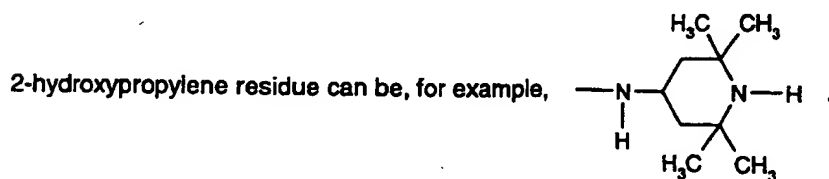
and the end group bonded to the diamino group can be, for example, hydrogen or a group

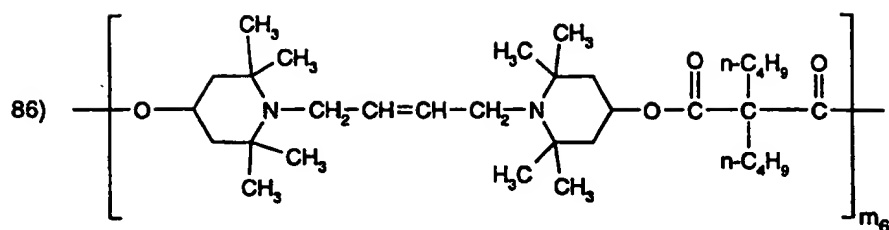


It may be convenient to replace the chlorine attached to the triazine by e.g. -OH or an amino group. Suitable amino groups are typically: pyrrolidin-1-yl, morpholino, -NH₂, -N(C₁-C₈alkyl)₂ and -NY'(C₁-C₈alkyl) wherein Y' is hydrogen or a group of the formula

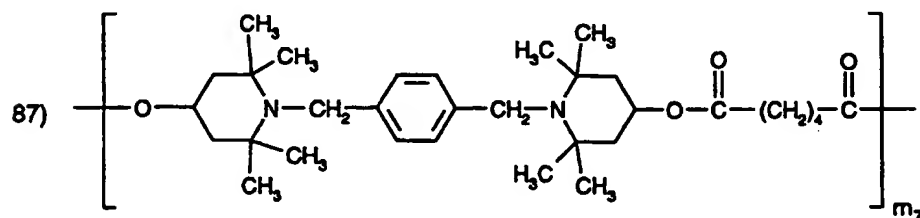


In the compound 85, the end group bonded to the 2,2,6,6-tetramethylpiperidin-4-ylamino residue can be, for example, hydrogen and the end group bonded to the

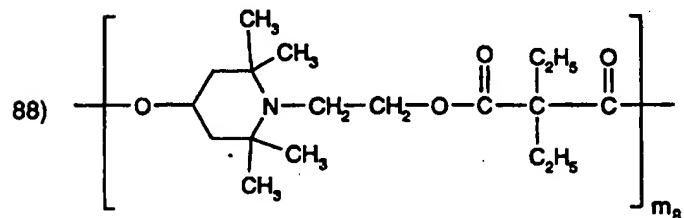
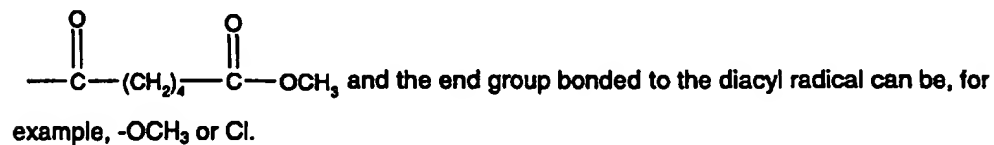




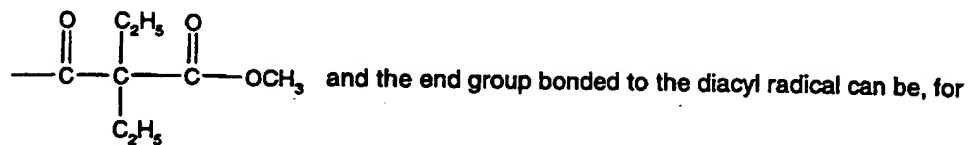
In the compound 86, the end group bonded to the -O- can be, for example, hydrogen or



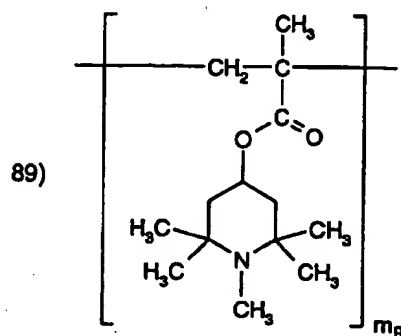
In the compound 87, the end group bonded to the -O- can be, for example, hydrogen or



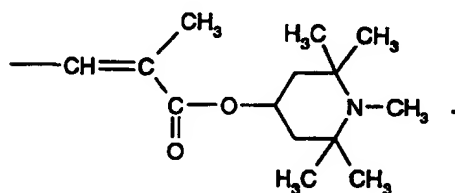
In the compound 88, the end group bonded to the -O- can be, for example, hydrogen or

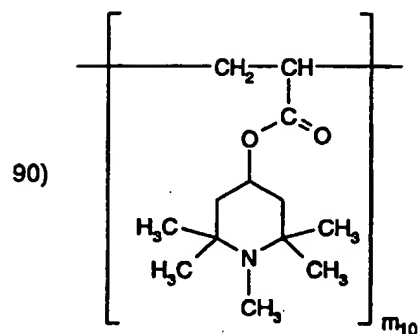


example, -OCH₃ or Cl.

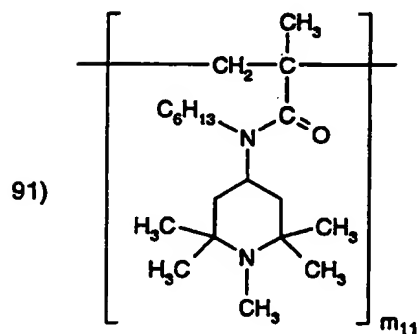
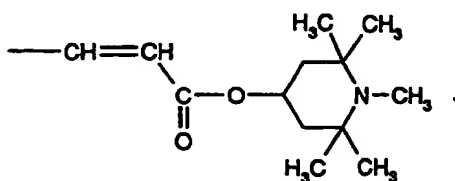


In the compound 89, the end group bonded to the -CH₂- can be, for example, hydrogen and the end group bonded to the ester residue can be, for example,

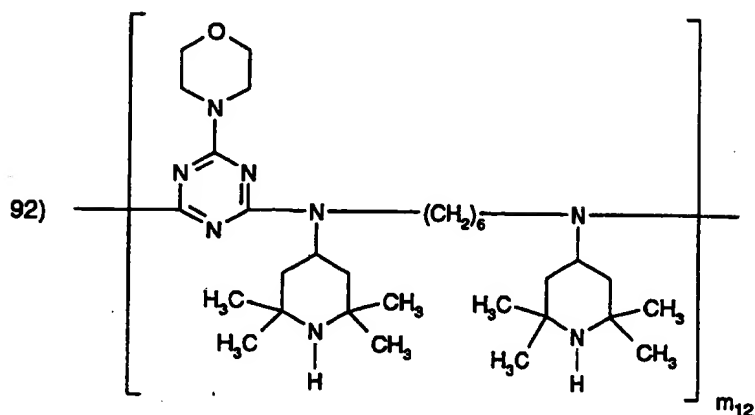
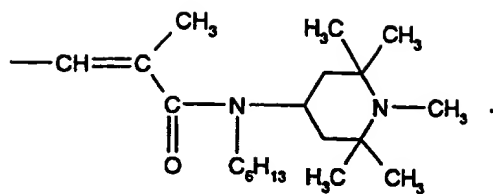




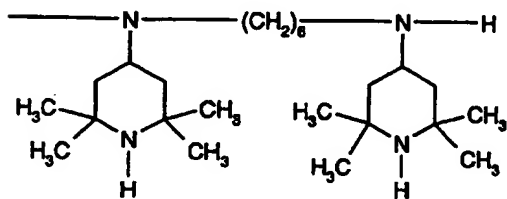
In the compound 90, the end group bonded to the $-\text{CH}_2-$ can be, for example, hydrogen and the end group bonded to the ester residue can be, for example,



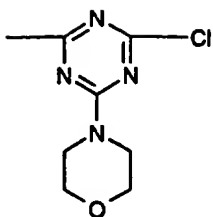
In the compound 91, the end group bonded to the $-\text{CH}_2-$ can be, for example, hydrogen and the end group bonded to the amide residue can be, for example,



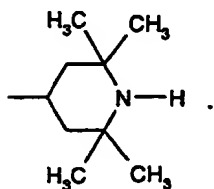
In the compound 92, the end group bonded to the triazine residue can be, for example, chlorine or a group



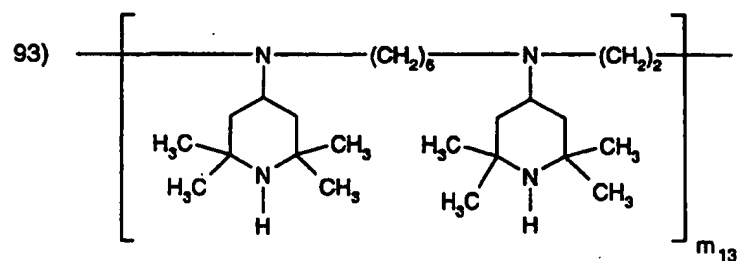
and the end group bonded to the diamino residue can be, for example, hydrogen or a group



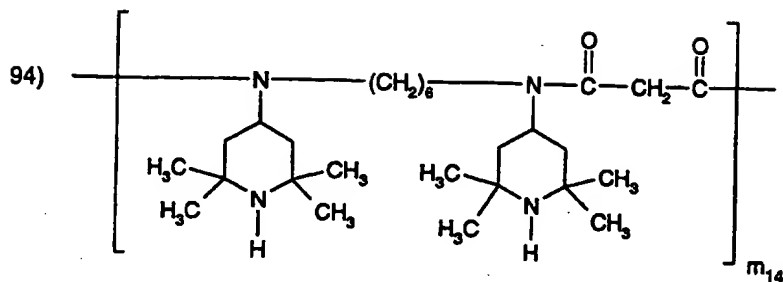
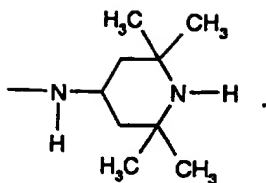
It may be convenient to replace the chlorine attached to the triazine by e.g. -OH or an amino group. Suitable amino groups are typically: pyrrolidin-1-yl, morpholino, -NH₂, -N(C₁-C₈alkyl)₂ and -NY'(C₁-C₈alkyl) wherein Y' is hydrogen or a group of the formula



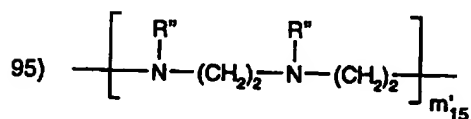
Preferred is also a compound which corresponds to compound 92 wherein the 2,2,6,6-tetramethyl-4-piperidyl groups are replaced by 1,2,2,6,6-pentamethyl-4-piperidyl groups.



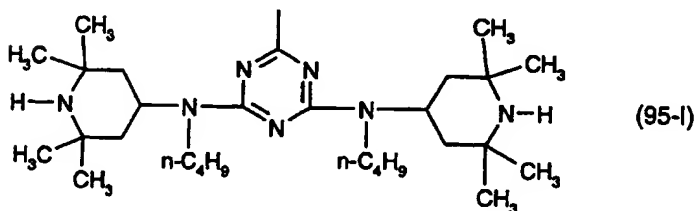
In the compound 93, the end group bonded to the diamino residue can be, for example, hydrogen and the end group bonded to the -CH₂CH₂- residue can be, for example,

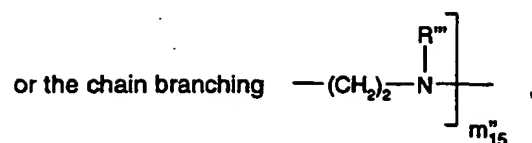


In the compound 94, the end group bonded to the diamino residue can be, for example, hydrogen and the end group bonded to the diacyl residue can be, for example, Cl.



in which R'' is a group of the formula



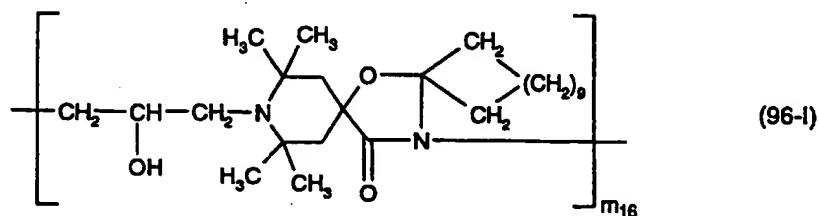


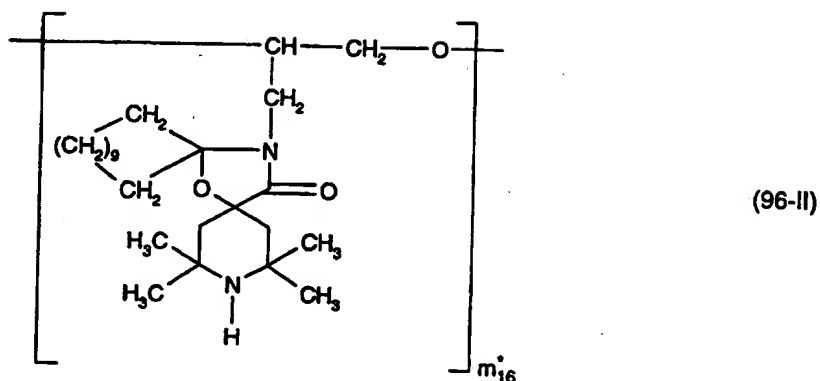
R''' is a group of the formula (95-I), and

m_{15}' and m_{15}'' are each a number from 0 to 200, preferably 0 to 100, in particular 0 to 50, with the proviso that $\text{m}_{15}' + \text{m}_{15}''$ is a number from 2 to 200, preferably 2 to 100, in particular 2 to 50. In the compound 95, the end group bonded to the diamino residue can be, for example, hydrogen and the end group bonded to the $\text{---CH}_2\text{CH}_2\text{---}$ group can be, for example, halogen, in particular Cl or Br.

Further examples for polymeric compounds are:

1) A compound of the formula (96-I) or (96-II)

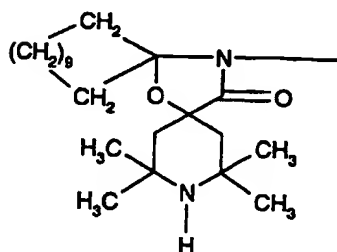




wherein m_{16} and m_{16}^* are a number from 2 to 50.

During the preparation, the compounds of the formulae (96-I) and (96-II) can be obtained together as a mixture and therefore, can also be employed as such. The (96-I):(96-II) weight ratio is, for example, from 20:1 to 1:20 or from 1:10 to 10:1.

In the compounds of the formula (96-I), the terminal group bonded to the nitrogen can be, for example, hydrogen and the terminal group bonded to the 2-hydroxypropylene radical can be, for example, a

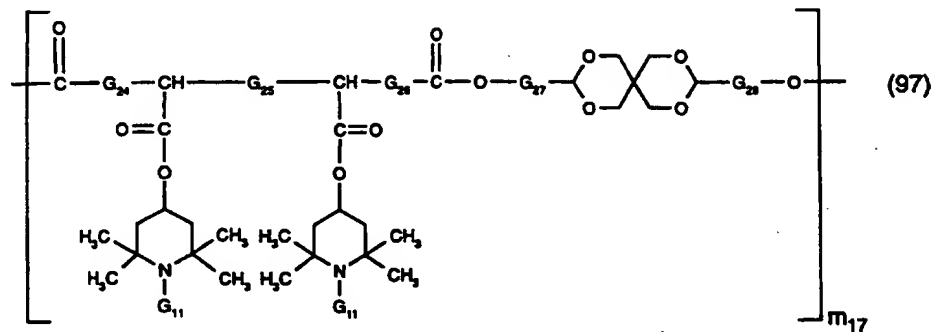


group.

In the compounds of the formula (96-II), the terminal group bonded to the dimethylene radical can be, for example, -OH, and the terminal group bonded to

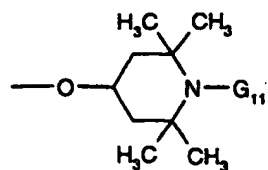
the oxygen can be, for example, hydrogen. The terminal groups can also be polyether radicals.

2) A compound of the formula (97)

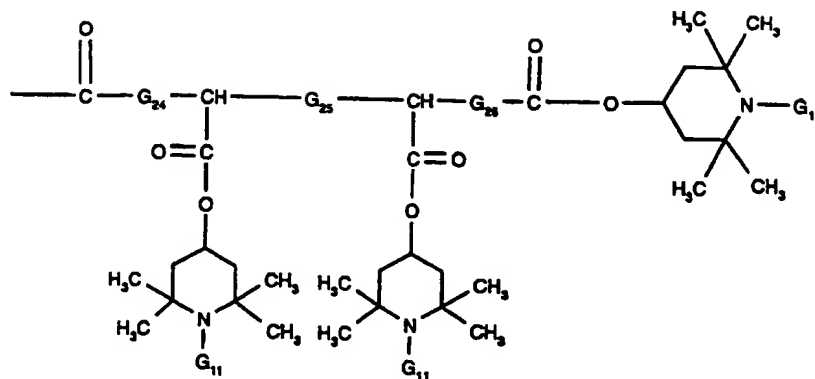


wherein G_{24} , G_{25} , G_{26} , G_{27} and G_{28} , independently of one another, are a direct bond or C_1 - C_{10} alkylene, G_{11} is as defined under (a') and m_{17} is a number from 1 to 50.

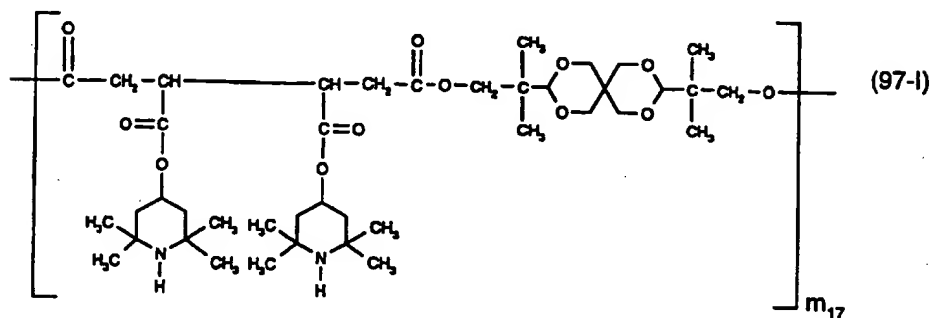
In the compound of the formula (97), the end group bonded to the $>C=O$ group can be, for example,



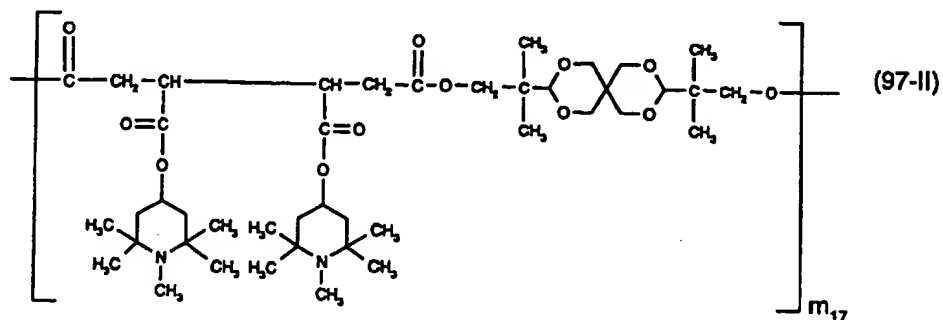
and the end group bonded to the oxygen can be, for example



Preferred are the following two compounds:

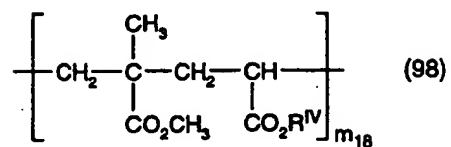


and

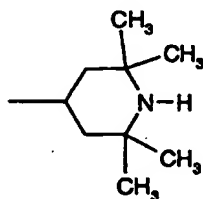


wherein the mean value of m_{17} is 2.5.

3) A compound of the formula (98)



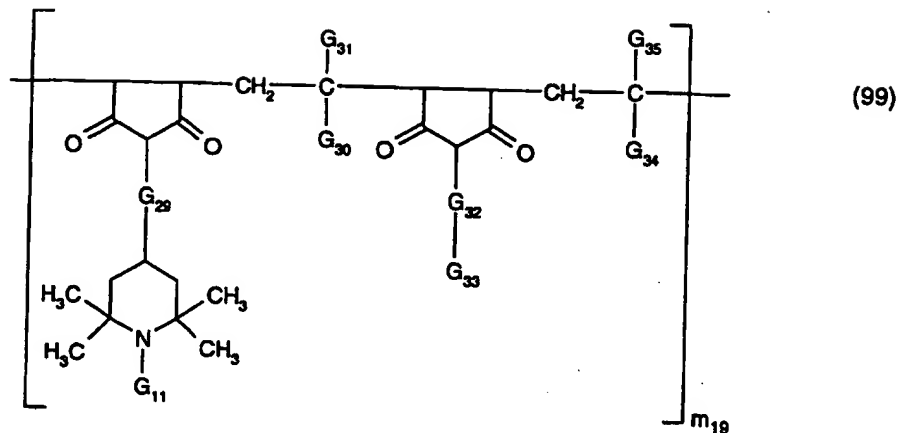
in which approximately one third of the radicals R^{IV} are $-\text{C}_2\text{H}_5$ and the others are a group



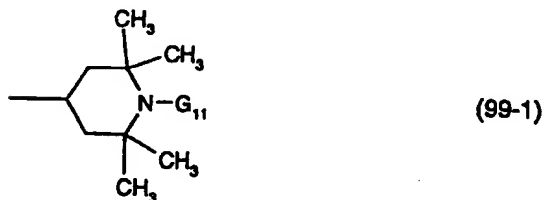
and m_{18} is a number in the range from 2 to 200, preferably 2 to 100, in particular 2 to 50.

In the compound (98), the end group bonded to the $-\text{CH}_2-$ residue can be, for example, hydrogen and the end group bonded to the $-\text{CH}(\text{CO}_2\text{R}^{\text{IV}})-$ residue can be, for example, $-\text{CH}=\text{CH}-\text{COOR}^{\text{IV}}$.

4) A compound of the formula (99)

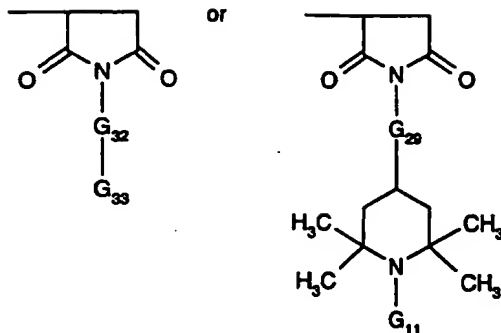


in which G_{11} is as defined under (a'), G_{29} and G_{32} , independently of one another, are a direct bond or a $-N(X_1)-CO-X_2-CO-N(X_3)-$ group, where X_1 and X_3 , independently of one another, are hydrogen, C_1-C_8 alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_9 phenylalkyl or a group of the formula (99-1)

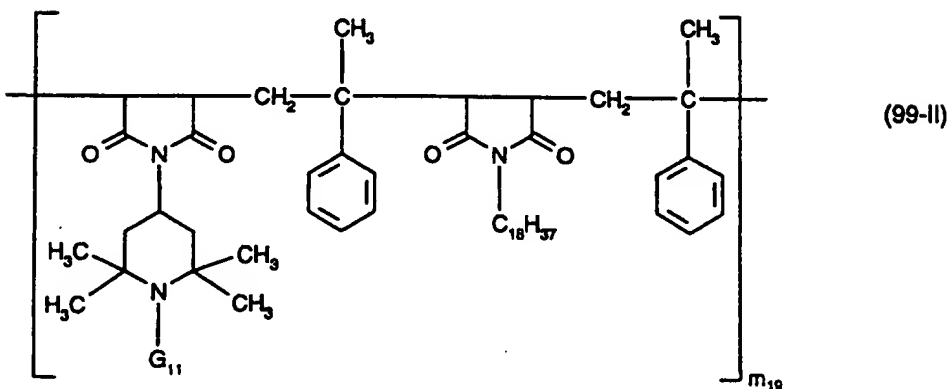
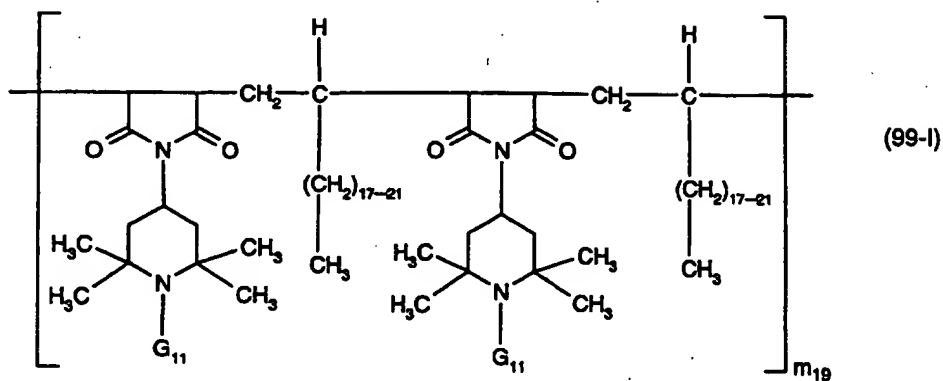


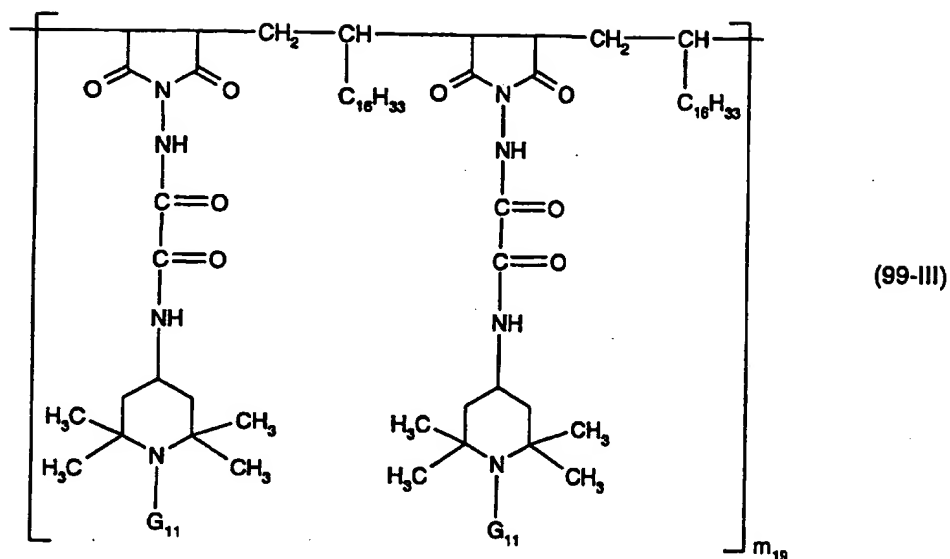
and X_2 is a direct bond or C_1-C_4 alkylene, G_{30} , G_{31} , G_{34} and G_{35} , independently of one another, are hydrogen, C_1-C_{30} alkyl, C_5-C_{12} cycloalkyl or phenyl, G_{33} is hydrogen, C_1-C_{30} alkyl, C_5-C_{12} cycloalkyl, C_7-C_9 phenylalkyl, phenyl or a group of the formula (99-1), and m_{19} is a number from 1 to 50.

In the compounds of the formula (99), the end group bonded to the 2,5-dioxopyrrolidine ring can be, for example, hydrogen, and the end group bonded to the $-C(G_{34})(G_{35})-$ radical can be, for example,



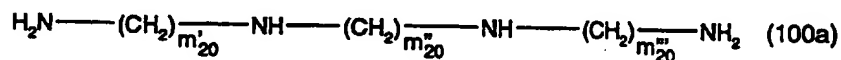
Examples of the compounds of the formula (99) are:





wherein G_{11} is hydrogen or methyl, and m_{19} is a number from 1 to 25.

5) A product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a) with cyanuric chloride, with a compound of the formula (100b)



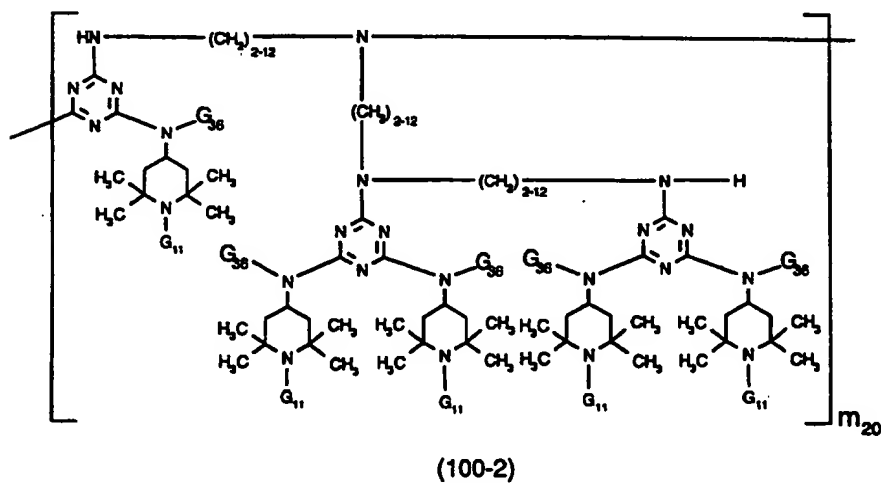
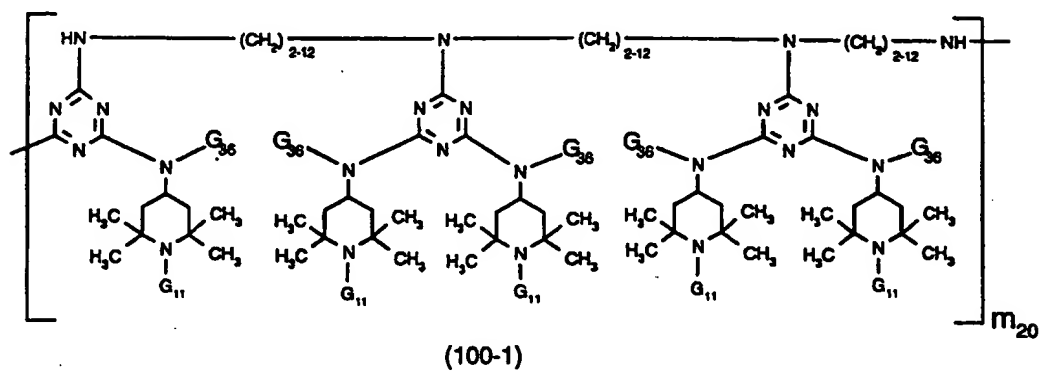
in which m'_{20} , m''_{20} and m'''_{20} , independently of one another, are a number from 2 to 12,

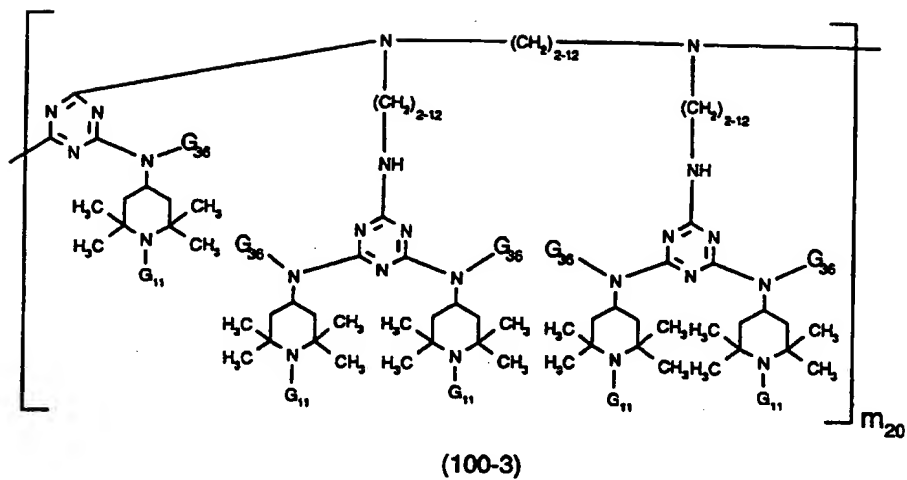
G_{36} is hydrogen, C_1 - C_{12} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl, and

G_{11} is as defined under (a'). A preferred product has the Chemical Abstracts-CAS No.

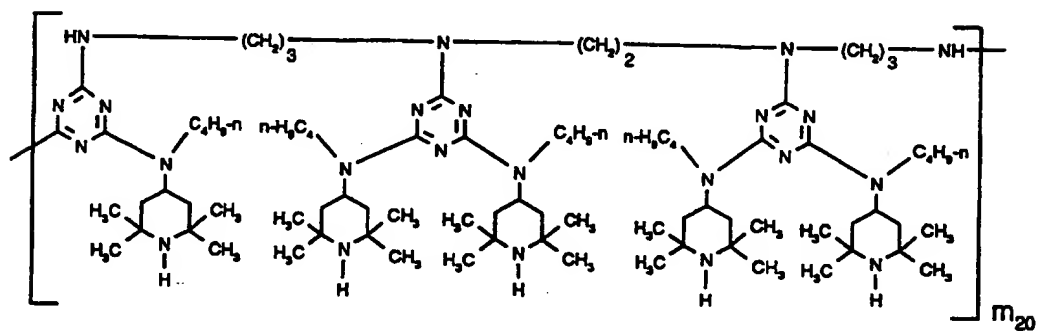
136 504-96-6 (Compound 100-A).

In general, the above reaction product can be represented for example by a compound of the formula 100-1, 100-2 or 100-3. It can also be in the form of a mixture of these three compounds.

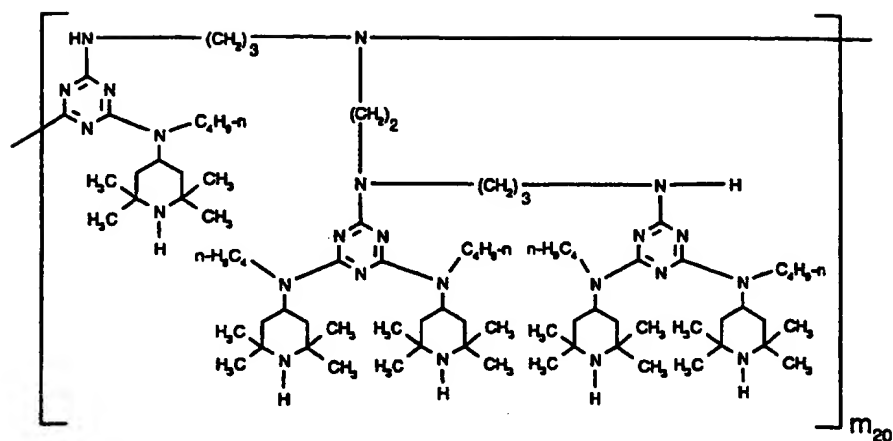




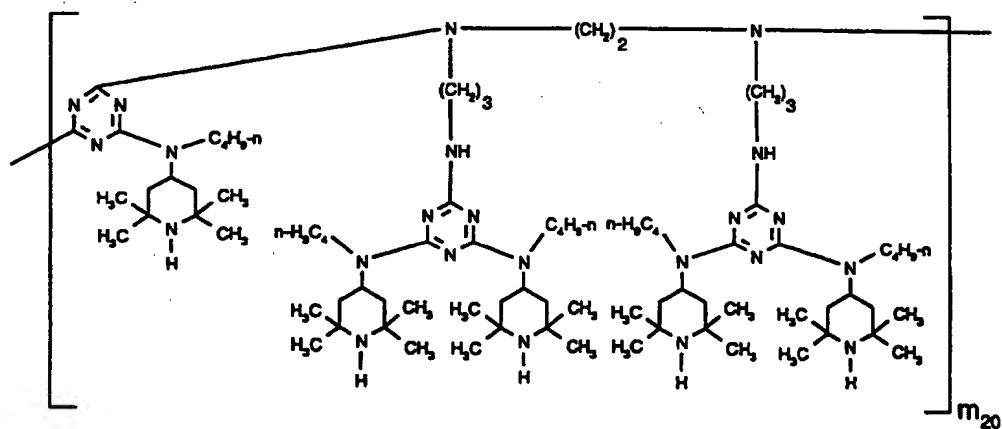
A preferred meaning of the formula (100-1) is



A preferred meaning of the formula (100-2) is

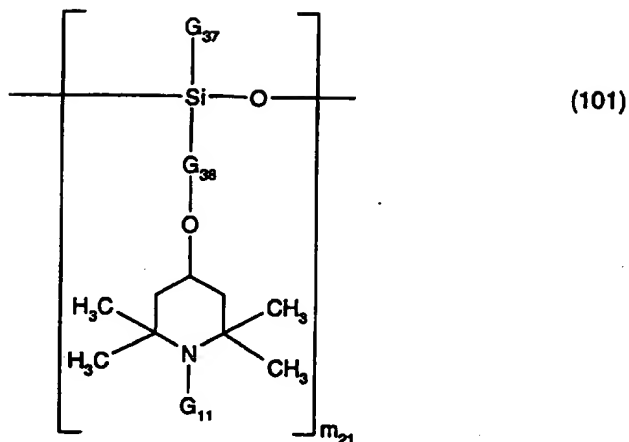


A preferred meaning of the formula (100-3) is



In the above formulae 100-1 to 100-3, m_{20} is preferably 1 to 20.

6) A compound of the formula (101)

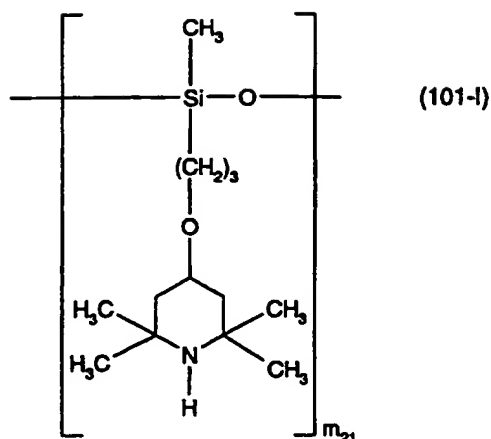


in which G_{11} is as defined under (a'), G_{37} is C_1 - C_{10} alkyl, C_5 - C_{12} cycloalkyl, C_1 - C_4 alkyl-substituted C_5 - C_{12} cycloalkyl, phenyl or C_1 - C_{10} alkyl-substituted phenyl, G_{38} is C_3 - C_{10} alkylene and m_{21} is a number from 1 to 50.

In the compounds of the formula (101), the terminal group bonded to the silicon atom can be, for example, $(G_{37})_3Si-O-$, and the terminal group bonded to the oxygen can be, for example, $-Si(G_{37})_3$.

The compounds of the formula (101) can also be in the form of cyclic compounds if m_{21} is a number from 3 to 10, i.e. the free valences shown in the structural formula then form a direct bond.

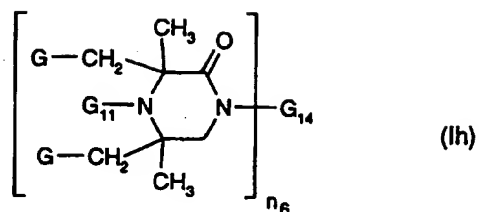
An example of a compound of the formula (101) is



with m_{21} being a number from 1 to 20.

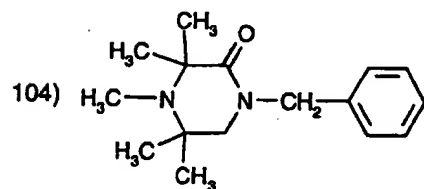
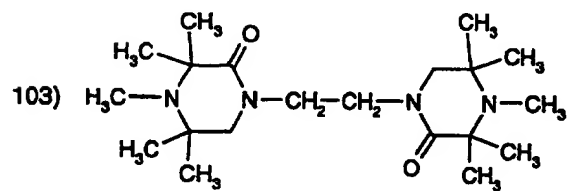
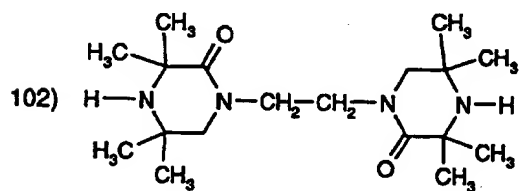
In the above shown oligomeric and polymeric compounds,
 examples of alkyl are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl and docosyl;
 examples of cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl;
 an example of C_7 - C_8 phenylalkyl is benzyl; and
 examples of alkylene are ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylhexamethylene, octamethylene and decamethylene.

(h') A compound of the formula (Ih)

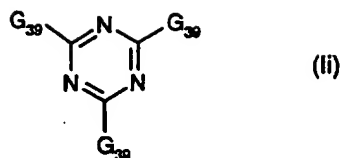


in which n_6 is the number 1 or 2, G and G_{11} are as defined under (a'), and G_{14} is as defined under (b'), but G_{14} cannot be $-\text{CONH-Z}$ and $-\text{CH}_2\text{-CH(OH)-CH}_2\text{-O-D-O-}$.

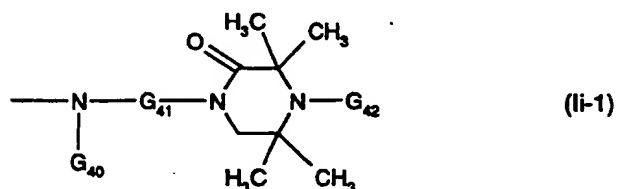
Examples of such compounds are the following:



(i') A compound of the formula (II)



wherein the radicals G_{39} , independently of one another, are a group of the formula (ii-1)



in which G_{40} is C_1 - C_{12} alkyl or C_5 - C_{12} cycloalkyl, G_{41} is C_2 - C_{12} alkylene and G_{42} is hydrogen, C_1 - C_8 alkyl, $-O-$, $-CH_2CN$, C_3 - C_6 alkenyl, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkyl which is substituted on the phenyl radical by C_1 - C_4 alkyl; or C_1 - C_8 acyl.

Alkyl is for example C_1 - C_4 alkyl, in particular methyl, ethyl, propyl or butyl.

Cycloalkyl is preferably cyclohexyl.

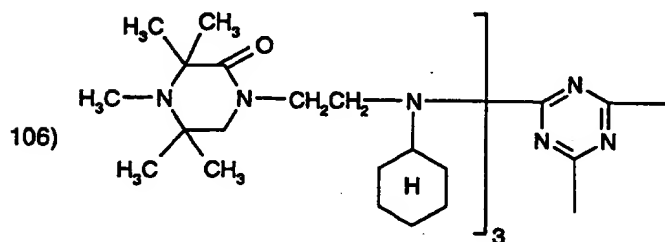
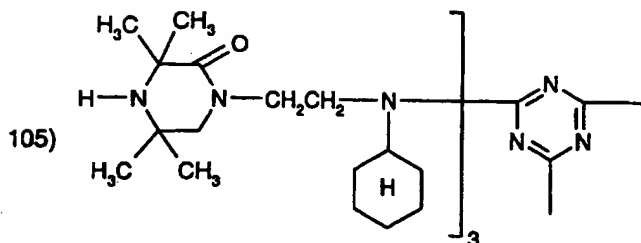
Alkylene is for example ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene or hexamethylene.

Alkenyl is preferably allyl.

Phenylalkyl is preferably benzyl.

Acyl is preferably acetyl.

Examples of compounds from this class are the compounds of the following formulae:



The sterically hindered amine compound (component (A)) is preferably one of the above compounds 1 to 106. The compounds 5, 10, 13, 14, 24, 25, 36-a, 36-b, 36-d, 49-a-I, 49-e, 63, 75, 76, 80-a, 81, 84-1, 84-2, 92, 93, 96-I, 96-II, 97-I, 97-II, 99-I, 100-A, 101-I, 105 and 106 are of interest. The compounds 13, 14, 36-a, 36-b, 36-d, 76, 81, 84-1, 96-I, 96-II, 100-A, 101-I, 105 and 106 are preferred. The compounds 13, 14, 36-d, 81, 84-1, 96-I, 96-II, 100-A, 101-I, 105 and 106 are particularly preferred.

Examples of an organic salt of Ca are Ca-stearate, Ca-laurate, Ca-lactate and Ca-stearoyl-lactate.

Examples of an inorganic salt of Ca are CaO and Ca(OH)₂.

The organic salt of zinc or magnesium defined in component (C) is preferably a compound of the formula MeL₂ in which Me is zinc or magnesium and L is an anion of an organic acid or of an enol. The organic acid can, for example, be a sulfonic acid, sulfinic acid, phosphonic acid or phosphinic acid, but is preferably a carboxylic acid. The acid can be aliphatic, aromatic, araliphatic or cycloaliphatic; it can be linear or branched; it can be substituted by

hydroxyl or alkoxy groups; it can be saturated or unsaturated and it preferably contains 1 to 24 carbon atoms.

Examples of carboxylic acids of this type are formic, acetic, propionic, butyric, isobutyric, caproic, 2-ethylcaproic, caprylic, capric, lauric, palmitic, stearic, behenic, oleic, lactic, ricinoleic, 2-ethoxypropionic, benzoic, salicylic, 4-butylbenzoic, toluic, 4-dodecylbenzoic, phenylacetic, naphthylacetic, cyclohexanecarboxylic, 4-butylcyclohexanecarboxylic or cyclohexylacetic acid. The carboxylic acid can also be a technical mixture of carboxylic acids, for example technical mixtures of fatty acids or mixtures of alkylated benzoic acids.

Examples of organic acids containing sulfur or phosphorus are methanesulfonic, ethanesulfonic, α,α -dimethylethanesulfonic, n-buthanesulfonic, n-dodecanesulfonic, benzenesulfonic, toluenesulfonic, 4-nonylbenzenesulfonic, 4-dodecylbenzenesulfonic or cyclohexanesulfonic acid, dodecanesulfonic, benzenesulfonic or naphthalenesulfonic acid, butylphosphonic acid, phenylphosphonic acid, monomethyl or monoethyl phenylphosphonate, monobutyl benzylphosphonate, dibutylphosphinic acid or diphenylphosphinic acid.

If L is an enolate anion, it is preferably an anion of a β -dicarbonyl compound or of an o-acylphenol. Examples of β -dicarbonyl compounds are acetylacetone, benzoylacetone, dibenzoylmethane, ethyl acetoacetate, butyl acetoacetate, lauryl acetoacetate or α -acetylcyclohexanone. Examples of o-acylphenols are 2-acetylphenol, 2-butyroylphenol, 2-acetyl-1-naphthol, 2-benzoylphenol or salicylaldehyde. The enolate is preferably the anion of a β -dicarbonyl compound having 5 to 20 carbon atoms.

Organic salts of zinc or magnesium are preferably an acetylacetonate or an aliphatic monocarboxylate having, for example, 1 to 24 carbon atoms. Magnesium acetate, laurate and stearate, zinc formate, acetate, oenanthatate, laurate and stearate as well as zinc acetylacetonate and magnesium acetylacetonate are some of the particular preferred examples.

Zinc stearate, magnesium stearate, zinc laurate, magnesium laurate, zinc acetylacetonate, magnesium acetylacetonate, zinc acetate and magnesium acetate are of special interest.

The inorganic salt of zinc or magnesium is for example zinc oxide, magnesium oxide, zinc hydroxide, magnesium hydroxide, or a carbonate containing compound such as

- Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, dolomite, e.g a Ca/Mg carbonate such as [®]Microdol Super from [®]Micro Minerals; or
- a natural or synthetic hydrotalcite.

The natural hydrotalcite is held to possess a structure $Mg_6Al_2(OH)_{16}CO_3 \cdot 4 H_2O$.

A typical empirical formula of a synthetic hydrotalcite is



Examples of the synthetic product include:



Preferred synthetic hydrotalcites are L-55R[®]II from [®]REHEIS as well as [®]ZHT-4A and [®]DHT-4A from [®]Kyowa Chemical Industry Co.

A preferred embodiment of this invention relates to a stabilizer mixture wherein component (C) is hydrotalcite, dolomite, Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, Zn-oxide, Mg-oxide, Zn-hydroxide, Mg-hydroxide, Zn-stearate, Mg-stearate, Zn-laurate, Mg-laurate, Zn-acetylacetonate, Mg-acetylacetonate, Zn-acetate or Mg-acetate.

The following combinations of components (B) and (C) are particularly preferred:

- Ca oxide and Mg stearate
- Ca oxide and Zn stearate
- Ca oxide and hydrotalcite ([®]DHT-4A)
- Ca hydroxide and Mg stearate
- Ca hydroxide and Zn stearate

A further preferred embodiment of this invention relates to a stabilizer mixture containing additionally

- (D1) a pigment or
- (D2) an UV absorber or
- (D3) a pigment and an UV absorber.

The pigment (component (D1)) may be an inorganic or organic pigment.

Examples of inorganic pigments are titanium dioxide, zinc oxide, carbon black, cadmium sulfide, cadmium selenide, chromium oxide, iron oxide, lead oxide and so on.

Examples of organic pigments are azo pigments, anthraquinones, phthalocyanines, tetrachloroisindolinones, quinacridones, isoindolines, perylenes, pyrrolopyrroles (such as Pigment Red 254) and so on.

All pigments described in "Gächter/Müller: Plastics Additives Handbook, 3rd Edition, Hanser Publishers, Munich Vienna New York", page 647 to 659, point 11.2.1.1 to 11.2.4.2 can be used as component (D1).

A particularly preferred pigment is titanium dioxide, optionally in combination with an organic pigment.

Examples of such organic pigments are:

C.I. (Colour Index) Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 155, C.I. Pigment Yellow 162, C.I. Pigment Yellow 168, C.I. Pigment Yellow 180, C.I. Pigment Yellow 183, C.I. Pigment Red 44, C.I. Pigment Red 170, C.I. Pigment Red 202, C.I. Pigment Red 214, C.I. Pigment Red 254, C.I. Pigment Red 264, C.I. Pigment Red 272, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 53:1, C.I. Pigment Red 57:1, C.I. Pigment Green 7, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:3 and C.I. Pigment Violet 19.

Examples of the UV absorber (component (D2)) are a 2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone, an ester of substituted or unsubstituted benzoic acid, an acrylate, an oxamide, a 2-(2-hydroxyphenyl)-1,3,5-triazine, a monobenzoate of resorcinol or a formamidine.

The 2-(2'-hydroxyphenyl)benzotriazole is e.g. 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxy-carbonylethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol] or the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_2$ where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl.

2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole and 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)-benzotriazole are preferred.

The 2-hydroxybenzophenone is for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy or 2'-hydroxy-4,4'-dimethoxy derivatives.

2-Hydroxy-4-octyloxybenzophenone is preferred.

The ester of a substituted or unsubstituted benzoic acid is for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate or 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2,4-Di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate are preferred.

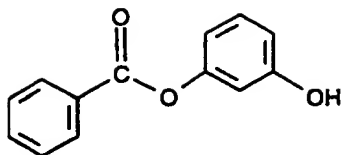
The acrylate is for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate or N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

The oxamide is for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide or its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide or mixtures of ortho- and para-methoxy-disubstituted oxanilides or mixtures of o- and p-ethoxy-disubstituted oxanilides.

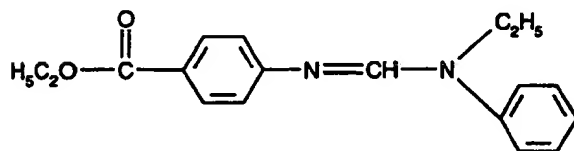
The 2-(2-hydroxyphenyl)-1,3,5-triazine is for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxy-propoxy)phenyl]-1,3,5-triazine or 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

2-(2-Hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine are preferred.

The monobenzoate of resorcinol is for example the compound of the formula



The formamidine is for example the compound of the formula



The UV absorber is in particular a

2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone or a hydroxyphenyltriazine.

The stabilizer mixture according to the present invention is useful for stabilizing polyolefins against degradation induced by light, heat or oxidation. Examples of suitable polyolefins are shown in the following.

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), branched low density polyethylene (BLDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually

have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π - or σ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

The invention therefore also relates to a composition containing a polyolefin and the stabilizer mixture as described herein and to a method for stabilizing a polyolefin against degradation induced by light, heat or oxidation, which comprises incorporating into the polyolefin the stabilizer mixture.

The polyolefins listed above under point 1 are preferred. Polyethylene and polypropylene as well as a polyethylene copolymer or a polypropylene copolymer are particularly preferred.

The invention furthermore relates to a composition comprising a polyolefin and a stabilizer mixture containing

- (A) a sterically hindered amine compound selected from the group consisting of the compounds 13, 14, 36-a, 36-b, 36-d, 96-I, 96-II, 100-A, 101-I, 105 and 106 as defined above;
- (B) an organic salt of Ca, in particular Ca-stearate, or an inorganic salt of Ca; and
- (C) an organic salt of Mg, an inorganic salt of Mg, an organic salt of Zn or an inorganic salt of Zn;

with the proviso that the polyolefin is polypropylene, when component (A) of the stabilizer mixture is the compound 96-I, 96-II or 100-A.

The components (A), (B), (C) and optionally (D1) and/or (D2) may be added to the polyolefin either individually or mixed with one another.

The sterically hindered amine compound (component (A)) is present in the polyolefin in an amount of preferably 0.01 to 5 %, in particular 0.01 to 1 % or 0.05 to 1 %, relative to the weight of the polyolefin.

The organic or inorganic salt of Ca (component (B)) is present in the polyolefin in an amount of preferably 0.005 to 5 %, in particular 0.02 to 0.5 %, relative to the weight of the polyolefin.

The organic or inorganic salt of Zn or Mg (component (C)) is present in the polyolefin in an amount of preferably 0.01 to 5 %, in particular 0.05 to 0.5 %, relative to the weight of the polyolefin.

The pigment (component (D1)) is optionally present in the polyolefin in an amount of preferably 0.01 to 10 %, in particular 0.05 to 1 %, relative to the weight of the polyolefin.

The UV absorber (component (D2)) is optionally present in the polyolefin in an amount of preferably 0.01 to 1 %, in particular 0.05 to 0.5 %, relative to the weight of the polyolefin.

The total amount of component (D3) (the pigment in combination with the UV absorber) is preferably 0.01 to 10 %, relative to the weight of the organic material. The weight ratio of the UV absorber to the pigment is for example 2:1 to 1:10.

When the pigment used is titanium dioxide in combination with an organic pigment as described above, titanium dioxide is preferably present in the organic material in an amount of 0.01 to 5 %, relative to the weight of the organic material, and the organic pigment may be present in an amount of, for example, 0.01 to 2 %, relative to the weight of the organic material.

The weight ratio of the components (A):(B) is preferably 20:1 to 1:5.

The weight ratio of the components (A):(C) is preferably 20:1 to 1:5.

The weight ratio of the components (A):(D1) is preferably 10:1 to 1:10.

The weight ratio of the components (A):(D2) is preferably 20:1 to 1:2.

The weight ratio of the components (A):(D3) is preferably 10:1 to 1:10.

The above components can be incorporated into the polyolefin by known methods, for example before or during shaping or by applying the dissolved or dispersed compounds to the polyolefin, if necessary with subsequent evaporation of the solvent. The components can be added to the polyolefin in the form of a powder, granules or a masterbatch, which contains these components in, for example, a concentration of from 2.5 to 25% by weight.

If desired, the components (A), (B), (C) and optionally (D1) and/or (D2) can be melt blended with each other before incorporation in the polyolefin. They can be added to the polyolefin before or during the polymerization or before the crosslinking.

The polyolefin stabilized according to this invention can be used in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or putties.

The stabilized polyolefin may additionally also contain various conventional additives, for example:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-

(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, Bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- und dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- und dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- und dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethyl-piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional

ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)-oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyl oxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-Isocetyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphite.

5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example, N-benzyl-alpha-phenyl-nitron, N-ethyl-alpha-methyl-nitron, N-octyl-alpha-heptyl-nitron, N-lauryl-alpha-undecyl-nitron, N-tetradecyl-alpha-tridecyl-nitron, N-hexadecyl-alpha-pentadecyl-nitron, N-octadecyl-alpha-heptadecyl-nitron, N-hexadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-pentadecyl-nitron, N-heptadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-hexadecyl-nitron, nitron derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example, diallyl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

9. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.

10. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers ("ionomers").

11. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and

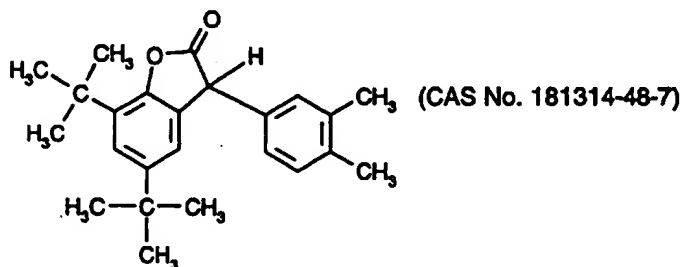
hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

12. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

13. Benzofuranones and indolinones, for example those disclosed in US-A-4325863, US-A-4338244, US-A-5175312, US-A-5216052, US-A-5252643, DE-A-4316611, DE-A-4316622, DE-A-4316876, EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

Particularly preferred conventional additives are those listed above under items 1 and/or 4.

Also the compound of the formula



is one of the preferred conventional additives which may additionally be incorporated into the polyolefin to be stabilized.

The weight ratio of the total amount of components (A), (B), (C) and optionally (D1) and/or (D2) to the total amount of the conventional additives can be, for example, 100:1 to 1:100.

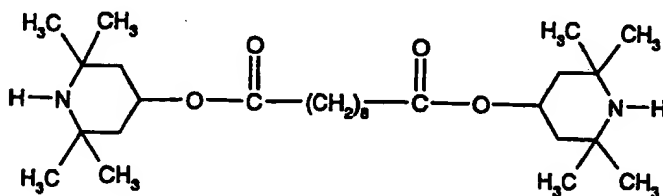
The examples below illustrate the invention in greater detail. All percentages and parts are by weight, unless stated otherwise.

Sterically hindered amine compounds used in the following Examples 1 to 3:

(For the polymeric compounds, the mean degree of polymerization is indicated in each case.)

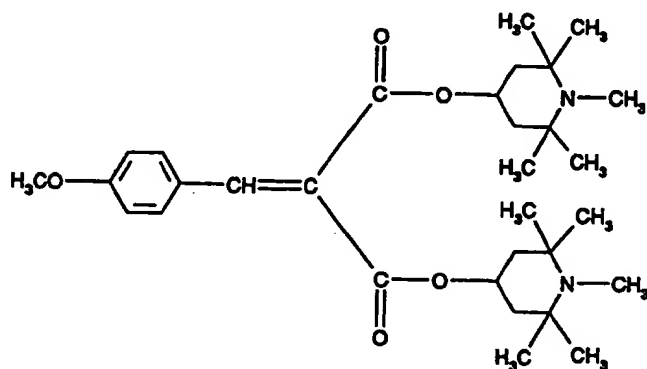
Compound 13:

([®]Tinuvin 770)



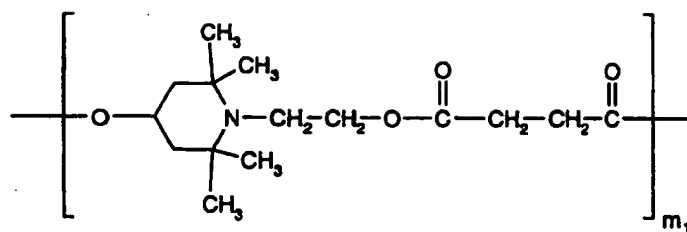
Compound 36-d:

([®]Sanduvor PR-31)



Compound 81:

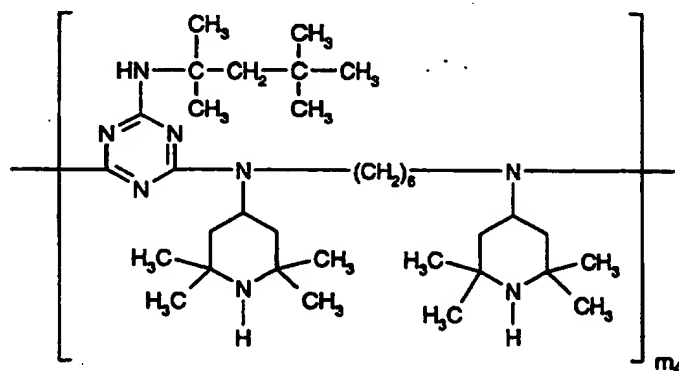
([®]Tinuvin 622)



with m_1 being 5.1.

Compound 84-1:

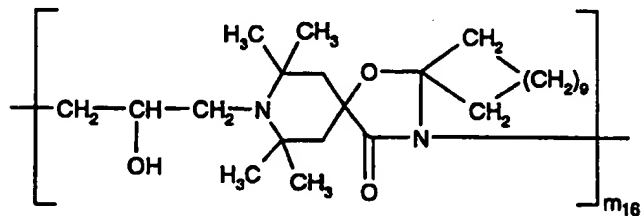
([®]Chimassorb 944)



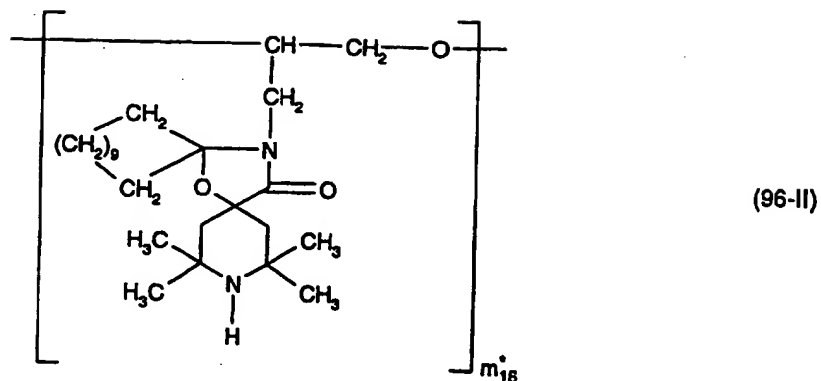
with m_4 being 4.5.

Mixture of the compounds 96-I and 96-II:

(Preferably [®]Hostavin N30)



(96-I)

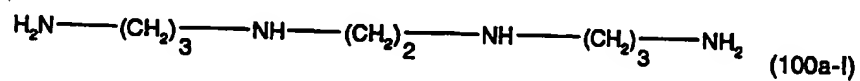


with m_{16} being 3.9 and m_{16}^* being 4.2 and the weight ratio of (96-I) to (96-II) being 4:1.

Compound 100-A:

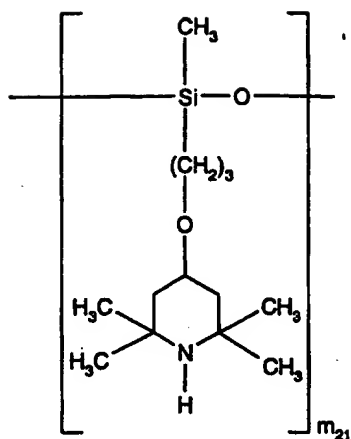
([®]Uvasorb HA88 (Chemical Abstracts CAS No. 136 504-96-6))

A product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a-I) with cyanuric chloride, with a compound of the formula (100b-I).



Compound 101-I:

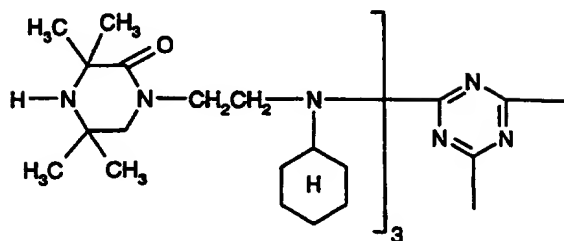
(Preferably [®]Uvasil 299)



with m_{21} being 5.8.

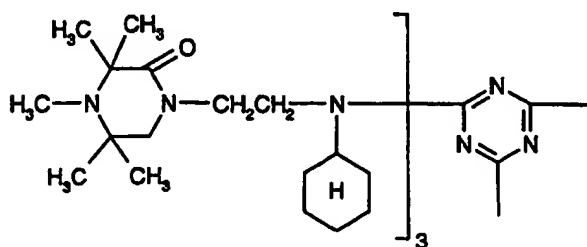
Compound 105:

(®Goodrite UV 3150)



Compound 106:

(®Goodrite UV 3159)



Example 1: Light stabilization of injection molded 2 mm polypropylene plaques.

100 parts of polypropylene powder (melt flow index: ~ 2.4 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 parts of tris[2,4-di-tert-butylphenyl] phosphite, and the stabilizer system indicated in Tables 1 to 3. Then, the blend is compounded in an extruder at temperatures of 200° - 220°C. The granules obtained on extrusion and granulation are transformed into 2 mm thick plaques at 240°-260°C in an automatic injection molding machine.

The plaques are mounted on sample holders and subjected to natural weathering in Florida (45° South, direct, approximately 140 kLy/year). Periodically, the carbonyl content of the samples is measured with an infrared spectrophotometer. The exposure time corresponding to formation of a carbonyl absorbance of 0.5 is a measure for the efficiency of the stabilizer system.

The values obtained are summarized in Tables 1 to 3.

The synergistic effect of the two coadditives ((1) and (2)) is determined by a comparison of the calculated $T_{0.5}$ value with the actually measured $T_{0.5}$ value. The $T_{0.5}$ values are calculated on the basis of the additivity law (B. Ranby and J.F. Rabek; Photodegradation, Photo-oxidation and Photostabilization of Polymers, Principles and Applications, John Wiley & Sons, London, New York, Sydney, Toronto, 1975, pages 418 and 419) according to the following equation:

$$\text{Expected stabilizing activity} = \frac{\text{Stabilizing activity of 100 \% (1)} + \text{stabilizing activity of 100 \% (2)}}{2}$$

There is a synergistic effect for the two coadditives in question, when $T_{0.5 \text{ measured}} > T_{0.5 \text{ calculated}}$.

Table 1:

Sterically hindered amine compound: 0.1 % of the compound 81

Coadditiv	T _{0.5} measured (kLy)	T _{0.5} calculated (kLy)
0.1 % of Ca-oxide	63	
0.1 % of Zn-hydroxide-carbonate	81	
0.05 % of Zn-hydroxide-carbonate + 0.05 % of Ca-oxide	86	72

Table 2:

Sterically hindered amine compound: 0.1 % of the compound 84-1

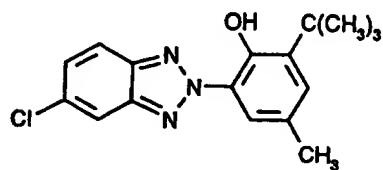
Coadditiv	T _{0.5} measured (kLy)	T _{0.5} calculated (kLy)
0.1 % of Ca-stearate	88	
0.1 % of Ca-oxide	150	
0.1 % of hydrotalcite (®DHT-4A)	144	
0.1 % of Zn-hydroxide-carbonate	136	
0.05 % of Ca-oxide + 0.05 % of hydrotalcite (®DHT-4A)	180	147
0.05 % of Zn-hydroxide-carbonate + 0.05 % of Ca-stearate	168	112
0.05 % of Zn-hydroxide-carbonate + 0.05 % of Ca-oxide	172	143

Table 3:

Sterically hindered amine compound: 0.05 % of the compound 81

UV absorber:

0.05 % of the compound of the formula



Coadditiv	T _{0.5} measured (kLy)	T _{0.5} calculated (kLy)
0.1 % of Ca-stearate	136	
0.1 % of Ca-oxide	102	
0.1 % of Ca-hydroxide	149	
0.1 % of hydrotalcite (®DHT-4A)	127	
0.1 % of Zn-hydroxide-carbonate	121	
0.1 % of Mg-stearate	216	
0.1 % of Zn-stearate	200	
0.1 % of Mg-acetylacetonate	202	
0.1 % of Mg-oxide	176	
0.1 % of Zn-oxide	70	
0.1 % of Mg-hydroxide	146	
0.1 % of dolomite (®Microdol Super)	77	
0.1 % of Zn-acetylacetonate	68	
0.05 % of hydrotalcite (®DHT-4A) + 0.05 % of Ca-oxide	116	114.5
0.05 % of Zn-hydroxide-carbonate + 0.05 % of Ca-stearate	182	128.5

0.05 % of Zn-hydroxide-carbonate + 0.05 % of Ca-oxide	175	111.5
0.05 % of dolomite (Microdol Super) + 0.05 % of Ca-stearate	112	106.5
0.05 % of Mg-stearate + 0.05 % of Ca-oxide	252	159
0.05 % of Mg-stearate + 0.05 % of Ca-hydroxide	222	182.5
0.05 % of Zn-stearate + 0.05 % of Ca-oxide	168	151
0.05 % of Mg-acetylacetonate + 0.05 % of Ca-oxide	240	152
0.05 % of Mg-acetylacetonate + 0.05 % of Ca-hydroxide	248	175.5
0.05 % of Zn-acetylacetonate + 0.05 % of Ca-oxide	97	85
0.05 % of Zn-acetylacetonate + 0.05 % of Ca-hydroxide	126	108.5
0.05 % of Mg-oxide + 0.05 % of Ca-oxide	148	139
0.05 % of Zn-oxide + 0.05 % of Ca-oxide	89	86
0.05 % of Ca-oxide + 0.05 % of Mg-hydroxide	137	124

Example 2: Light stabilization of polypropylene tapes.

100 parts of polypropylene powder (melt flow index: 2 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 parts of tris[2,4-di-tert-butylphenyl] phosphite and the stabilizer system indicated in Table 4. Then, the blend is compounded in an extruder at temperatures of 180°- 220°C. The granules obtained on extrusion and granulation are transformed into films at 220°-260°C in a second extruder equipped with a flat sheet die. The

films are cut into ribbons which are drawn to achieve a stretch ratio of 1:6. The tapes obtained with this procedure are finally 50 μm thick and 2.5 mm wide.

The tapes are mounted without tension on sample holders and exposed in a WEATHER-OMETER Ci 65 (black panel temperature $63 \pm 2^\circ\text{C}$, without water-spraying). Periodically, the tensile strength of the exposed tapes is measured. The exposure time corresponding to a loss of 50 % (T_{50}) of the initial tensile strength is a measure for the efficiency of the stabilizer system.

The values obtained are summarized in Table 4.

The determination of the synergistic effect of the two coadditives is carried out as described in Example 1.

Table 4:

0.4 % of titanium dioxide (rutile)

Sterically hindered amine compound	$T_{50 \text{ measured}}$ (hours to 50 % retained tensile strength)			
	0.05 % of Ca-stearate + 0.05 % of hydrotalcite (®DHT-4A)	0.1 % of Ca-stearate	0.1 % of hydrotalcite (®DHT-4A)	$T_{50 \text{ calculated}}$
0.05 % of compound 13	3360	2150	1920	2035
0.10 % of compound 13	7600	5600	4300	4950
0.20 % of compound 13	14500	13500	10000	11750

Example 3: Light stabilization of compression molded 0.5 mm polypropylene copolymer films

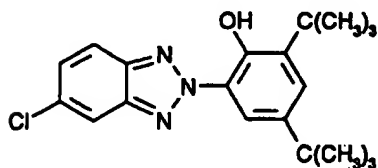
100 parts of unstabilized polypropylene powder (melt flow index: ~ 6 g/10 min at 230°C and 2160 g) are homogenized at 200°C for 10 min in a Brabender plastograph with 0.05 parts of pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.10 parts of tris[2,4-di-tert-butylphenyl] phosphite, and the stabilizer system indicated in Tables 5 to 8. The material thus obtained is compression molded in a laboratory press between two aluminum foils for 6 min at 260°C to a 0.5 mm thick film which is cooled immediately to room temperature in a water-cooled press. Samples of 60 mm x 25 mm are cut out of these 0.5 mm films and exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer. The exposure time corresponding to formation of a carbonyl absorbance of 0.1 is a measure for the efficiency of the stabilizer system. The values obtained are summarized in Tables 5 to 8.

Table 5:

0.1 % of Ca-stearate,

0.1 % of Mg-stearate and

0.1 % of the compound of the formula



0.1 % of sterically hindered amine compound	T _{0.1} (h)
Compound 101-I	3680
Compound 100-A	3200
Mixture of compounds 96-I and 96-II	2480

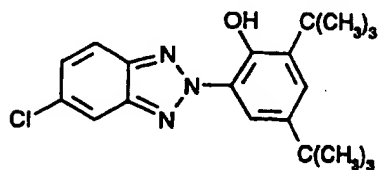
Compound 105	2920
Compound 106	2600
Compound 36-d	3080

Table 6:

0.1 % of Ca-stearate,

0.1 % of hydrotalcite ([®]DHT-4A) and

0.1 % of the compound of the formula



0.1 % of sterically hindered amine compound	T0.1 (h)
Compound 101-I	3680
Compound 100-A	3460
Compound 106	4400

Table 7:

0.1 % of Ca-stearate,

0.1 % of Mg-stearate and

0.5 % of TiO₂ (rutile)

0.1 % of sterically hindered amine compound	T0.1 (h)
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Compound 101-I	4530
Compound 100-A	3340
Compound 105	3280
Compound 106	3320
Compound 36-d	3340

Table 8:

0.1 % of Ca-stearate,
0.1 % of hydrotalcite (®DHT-4A) and
0.1 % of TiO₂ (rutile)

0.1 % of sterically hindered amine compound	T0.1 (h)
Compound 101-I	4120
Compound 100-A	4080
Compound 105	3905
Compound 106	3955

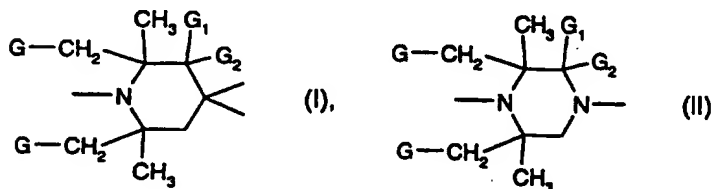
Claims

1. A stabilizer mixture containing

- (A) a sterically hindered amine compound,
- (B) an organic salt of Ca or an inorganic salt of Ca and
- (C) an organic salt of Mg, an inorganic salt of Mg, an organic salt of Zn or an inorganic salt of Zn;

with the proviso that component (C) is Mg-hydroxide-carbonate, Zn-hydroxide-carbonate or dolomite, when component (B) is calcium stearate.

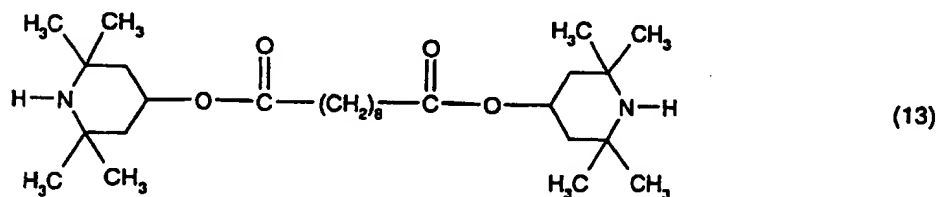
2. A stabilizer mixture according to claim 1 wherein the sterically hindered amine compound corresponds to a compound containing at least one group of the formula (I) or (II)

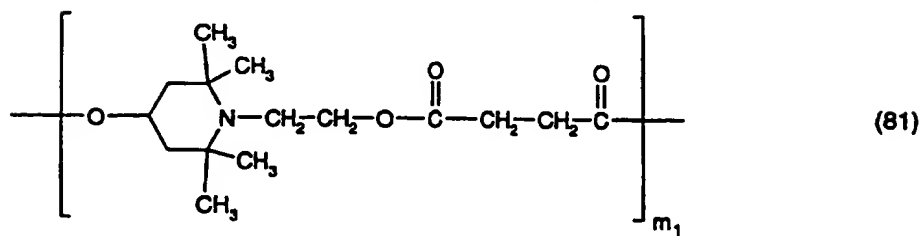
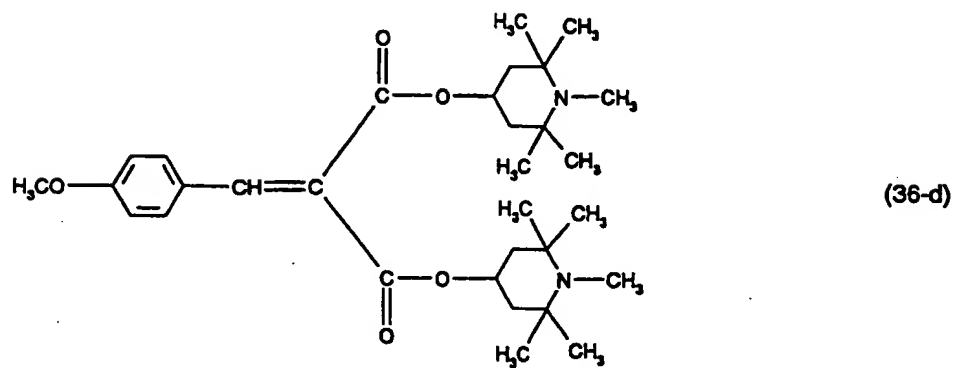
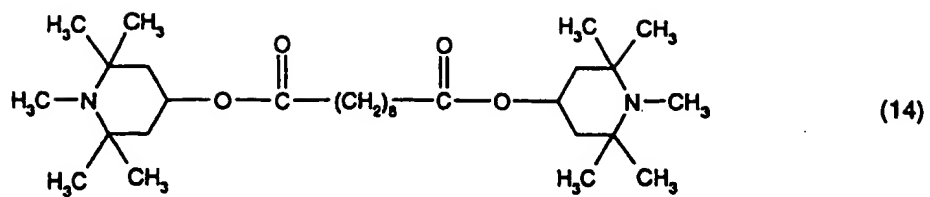


in which G is hydrogen or methyl, and

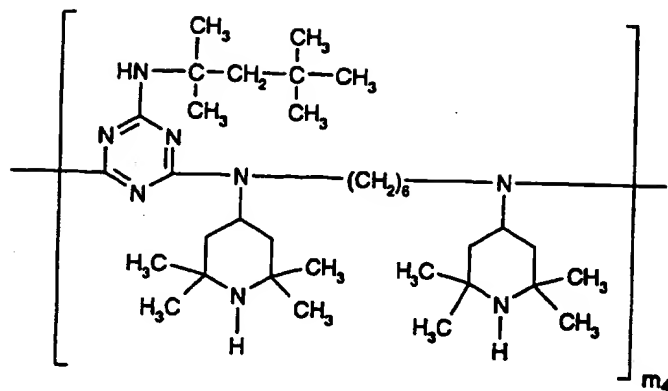
G₁ and G₂, independently of one another, are hydrogen, methyl or together are a substituent =O.

3. A stabilizer mixture according to claim 1, wherein the sterically hindered amine compound is



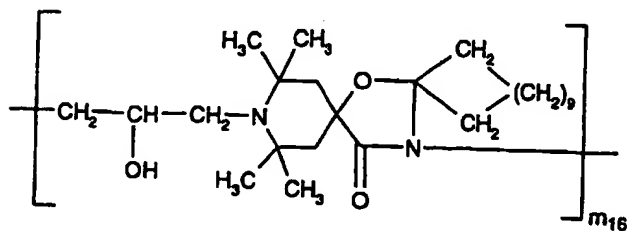


with m_1 being 5.1;

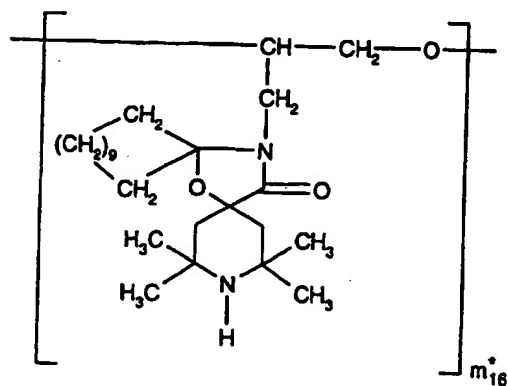


(84-1)

with m_4 being 4.5;

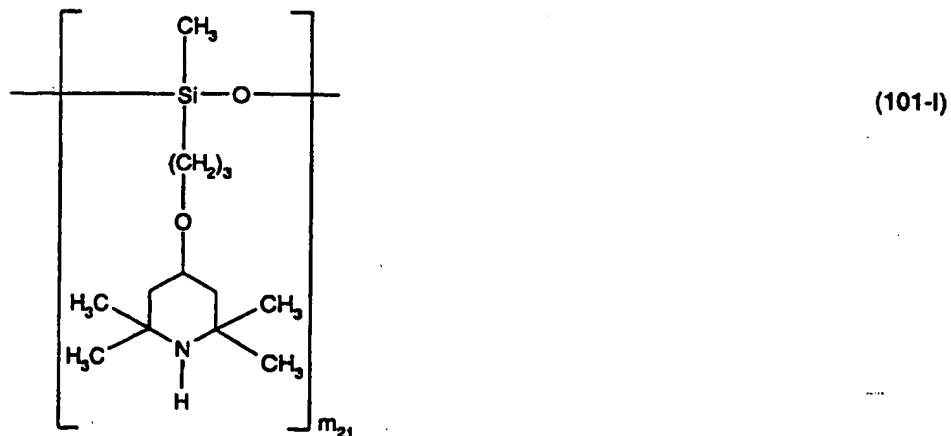
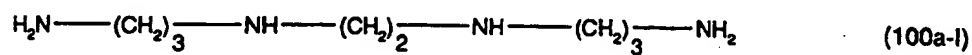


(96-I)

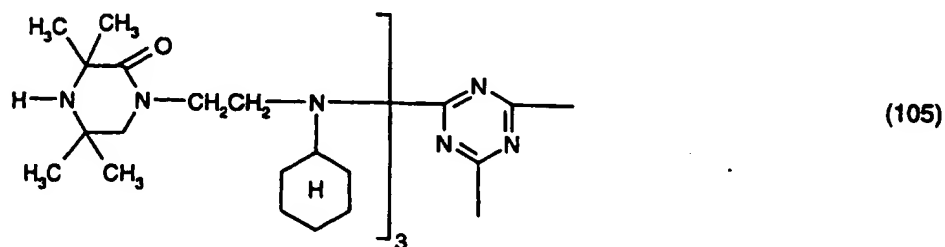


(96-II)

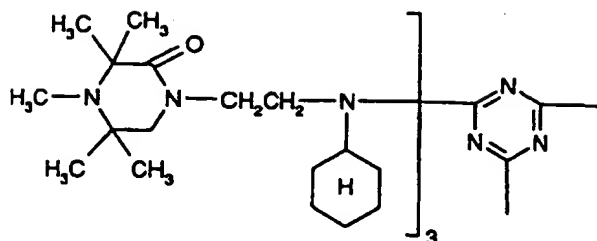
a product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a-I) with cyanuric chloride, with a compound of the formula (100b-I),



with m_{21} being 5.8;



or



(106).

4. A stabilizer mixture according to claim 1 wherein the organic salt of Ca is Ca-stearate, Ca-lactate or Ca-stearoyl-lactate and the inorganic salt of Ca is Ca-oxide or Ca-hydroxide.
5. A stabilizer mixture according to claim 1 wherein component (C) is hydrotalcite, dolomite, Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, Zn-oxide, Mg-oxide, Zn-hydroxide, Mg-hydroxide, Zn-stearate, Mg-stearate, Zn-laurate, Mg-laurate, Zn-acetylacetonate, Mg-acetylacetonate, Zn-acetate or Mg-acetate.
6. A stabilizer mixture according to claim 1, wherein
 component (B) is Ca oxide and component (C) is Mg stearate,
 component (B) is Ca oxide and component (C) is Zn stearate,
 component (B) is Ca oxide and component (C) is hydrotalcite,
 component (B) is Ca hydroxide and component (C) is Mg stearate, or
 component (B) is Ca hydroxide and component (C) is Zn stearate.
7. A stabilizer mixture according to claim 1, containing additionally
 (D1) a pigment or
 (D2) an UV absorber or
 (D3) a pigment and an UV absorber.
8. A stabilizer mixture according to claim 7 wherein the pigment is titanium dioxide, zinc oxide, carbon black, cadmium sulfide, cadmium selenide, chromium oxide, iron oxide, lead oxide, an azo pigment, an anthraquinone, a phthalocyanine, a tetrachloroisindolinone, a quinacridone, an isoindoline, a perylene or a pyrrolopyrrole.
9. A stabilizer mixture according to claim 7 wherein the UV absorber is

a 2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone, an ester of substituted or unsubstituted benzoic acid, an acrylate, an oxamide, a 2-(2-hydroxyphenyl)-1,3,5-triazine, a monobenzoate of resorcinol or a formamidine.

10. A composition comprising a polyolefin and a stabilizer mixture according to claim 1.

11. A composition according to claim 10 wherein the polyolefin is polyethylene, polypropylene, a polyethylene copolymer or a polypropylene copolymer.

12. A composition comprising a polyolefin and a stabilizer mixture containing

(A) a sterically hindered amine compound selected from the group consisting of the compounds 13, 14, 36-a, 36-b, 36-d, 96-I, 96-II, 100-A, 101-I, 105 and 106 as defined in claim 3;

(B) an organic salt of Ca or an inorganic salt of Ca; and

(C) an organic salt of Mg, an inorganic salt of Mg, an organic salt of Zn or an inorganic salt of Zn;

with the proviso that the polyolefin is polypropylene, when component (A) of the stabilizer mixture is the compound 96-I, 96-II or 100-A.

13. A method for stabilizing a polyolefin against degradation induced by light, heat or oxidation, which comprises incorporating into the polyolefin a stabilizer mixture according to claim 1.



The
Patent
Office
83

Application No: GB 9827565.4
Claims searched: 1 to 11 and 13

Examiner: Miss M M Kelman
Date of search: 13 April 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): C3K KCZ

Int CI (Ed.6): C08K 5/00, 5/098, 5/34, 5/3432, 5/3435, 5/3437, 5/3492

Other: ONLINE: EDOC, PAJ, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0429731 A1 AT PLASTICS see Examples 9 and 10	1,2,5,7,10,11,13
X	EP 0212559 A2 ADEKA ARGUS see Controls 4 and 5 in Tables I to III, Control 3 in Table IV and Examples 1 to 26	1,2,3,5,7
X	US 5350785 A CIBA-GEIGY see the claims and column 27, lines 22 to 50	1,2,5
X	US 5283273 A CIBA-GEIGY see the claims and column 21, lines 37 to 51	1,2,5
X	US 5025051 A FERRO see Examples 13 to 17,20,23,32 and 41 to 44	1,2,7,10,11,13

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.